

Four out-of-equilibrium stories

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von M.Sc. Gianmaria Falasco

geboren am 02.12.1988 in Padova, Italien.

Gutachter:

Prof. Dr. Klaus Kroy, Universität Leipzig

Prof. Dr. Massimiliano Esposito, Université du Luxembourg

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Abstract

This thesis collects the published papers of ours on the subject of classical nonequilibrium statistical mechanics. Mainly stochastic systems are considered, with special regard to applications in soft matter physics.

First, we study Brownian motion in a bath driven far from equilibrium by a thermal gradient, for which we derive the appropriate generalized Langevin description and extended fluctuation-dissipation relation. We then move to Markovian systems driven by non-conservative forces and simultaneously in contact with multiple heat baths. Their steady states are found to be characterized by virial relations and generalized equations of state that feature dissipative currents on the same footing with thermodynamic variables. Then, the dynamical properties of such systems are addressed. We extend nonequilibrium linear response theory to thermal perturbations, which allows to extract thermal susceptibilities—key quantities in the construction of a general thermodynamic theory—from unperturbed fluctuations. Finally, we turn to the fluctuation theorems, i.e., symmetries that hold for the statistics of typical nonequilibrium quantities, such as entropy production and currents. We show that they are in practice valid beyond their expected range of application and extend them to other meaningful observables.

Each of the four chapters includes a short informal introduction to the matter. It provides the specific background—which a nonspecialist might be unfamiliar with—needed in reading the associated papers. What they lack in rigor is (hopefully) made up in simplicity, leaving us free to focus on concepts.

Contents

1	Introduction	4
2	Brownian motion in a temperature gradient	1
3	Nonequilibrium virial relations and generalized equation of state	25
4	Nonequilibrium linear response theory	46
5	Fluctuation theorems	87
	Author contributions	123
	Acknowledgments	125

Chapter 1

Introduction

Systems composed of many interacting degrees of freedom are typically intractable in full detail. An explicit solution of their dynamical equations of motion is not only unattainable but, if miraculously found, it would hardly reveal anything of the interesting physics [1, 2]. The reason being that the higher-level qualities of any physical system are collective, emerging phenomena, that in general cannot be deduced from the microscopic laws [3, 4]. Luckily, the existence of inherent (time and length) scale separations selects, among the multitude of degrees of freedom, the few relevant ones we (as macroscopic systems) eventually couple with. This very point opens the way for describing physical systems in terms of a handful of coarse-grained variables, which turn out to follow the universal laws of Thermodynamics. Statistical Mechanics then bridges the gap between micro- and macroscale: it explains how these typical laws emerge from the microscopic chaotic behavior when the microstates are justly regarded as random variables.

For systems in thermodynamic equilibrium, i.e. without any macroscopic current (of mass, energy etc.), statistical mechanics provides a probabilistic descriptions recurring to minimal assumptions, namely, the microstates of constant energy are equally probable. When the relevant external constraints and physical invariants (e.g. volume, particle number) are considered, the framework yields the probability distribution of the system states [5, 6]. The equilibrium statistical theory may be depicted as the slide-down from this summit¹ [8]. Ensemble distributions allow for calculating the probability of macroscopic fluctuations and, additionally, determine the symmetries their time evolution satisfies [9]—such as the fluctuation-dissipation theorem that will be discussed in Chapter 2. Its practical implementation is strewed with technical difficulties, but its core principles are justified by a century-long history of experimental evidences [10].

On the contrary, for nonequilibrium systems, i.e. those run through by macroscopic currents², a route to the summit is still to be set. More precisely, there is no general principles to calculate the probability of the system states, and thus of the physical observables from the sole knowledge of the system constraints or invariants³ [12]. Finding such overarching principles is likely to have far reaching impacts, as nonequilibrium conditions are ubiquitous in Nature. They encompass a myriad of phenomena from

¹The climb-up, i.e. the foundational aspects of the theory, are yet under debate [7].

²This might happen because some external constraint either is removed (leading the system to relax to a new equilibrium) or causes sustained dissipation.

³Exceptions are, e.g., integrable systems. They are describable by generalized Gibbs ensembles which include the local conserved quantities as additional constraints [11].

the subnuclear to the cosmological scale⁴, passing through the “middle world” [14], i.e. the mesoscale in which units are too large to experience quantum effects but too small to be described in a purely deterministic fashion. Among its many inhabitants, there appear the basic constituents of life (from biological macromolecules to cells), arguably the most striking examples of the complexity nonequilibrium can bring about.

Although a unifying theoretical framework is still missing, a number of general results is now starting to shed light on the richness of nonequilibrium physics. Progress has been achieved in the last decades on different subjects⁵: the study of fluctuations and their symmetry properties [15, 16], e.g. expressed by the so-called fluctuation theorems [17, 18]—which lend themselves naturally to be described by the theory of large deviations [19]; the thermodynamics of small systems and chemical reactions [18, 20, 21], where fluctuations of heat, work and entropy are considered and the thermodynamic role of information (acquired and consumed by measurements, feedback and erasure procedures) is explicated [22]; the physical aging of systems with complex energy landscape [23] and the approach to (effective emergence of) equilibrium in systems initially prepared in non-thermal states [24–27].

Alongside these elemental topics, the understanding of paradigmatic complex phenomena represents an equally fundamental line of research. Among them we may cite nonequilibrium phase transitions and the existence of universality classes [28, 29]; the hydrodynamic properties, self-organization and pattern formation of active (i.e. energy-consuming) matter [30]; the anomalous transport in low dimensional systems [31], and crowded, random or fractal environments [32–36]; (the longstanding problem of) turbulence in fluids [37].

Advances in many areas have been made through the study of specific model systems [38, 39] which are believed to capture the dominant mechanisms at play out of equilibrium. The emerging picture reveals the role of irreversibility in generating effective long-range interactions, spontaneous symmetry breaking and universal power-law distributions for macroscopic observables, just to cite a few instances.

Some putative criteria (e.g. maximum entropy production [40], superstatistics [41]) and mechanisms (e.g. self-organized criticality [42] and bistability [43]) have been proposed, which partly comply with these evidences. It is fair to say, though, that the lack of a solid theoretical basis⁶ for their (limited) empirical effectiveness relegates them to the status of conjectures.

The contributions of this thesis find their place in this broad scenario. We begin in Chapter 2 with Brownian motion in a nonisothermal fluid to address the problem of deriving an appropriate description of nonequilibrium fluctuations when no equilibrium thermal bath exists. Starting from the fluctuating hydrodynamics of the solvent coupled to a suspended particle, we derive the generalized Langevin equation and noise statistics for the particle alone [46]. Integrating out the solvent’s superfluous degrees of freedom yields a remarkable generalization of the fluctuation-dissipation theorem featuring a

⁴Even the cosmic microwave background, often presented as the most iconic example of black body radiation in the Universe, possesses some unexplained nonequilibrium features represented by an excess temperature of its low frequencies [13]

⁵This partial, randomly ordered list is unintentionally biased by the limited knowledge of the author and the current fashionability of the topics.

⁶Sometimes there appear inconsistencies between detached research lines. Consider, e.g., the maximum entropy production principle, which is a proposed algorithm for constructing a probability distribution from available information by maximizing the Gibbs-Shannon entropy subject to various constraints. By construction, it neglects non-dissipative dynamical aspects (unless they are introduced via the constraints, which then makes the theory of very limited utility [44]), in plain contradiction with fluctuation theory, which predicts them to be of crucial importance far from equilibrium [45].

frequency-dependent noise temperature, which was previously postulated to govern the linear response away from equilibrium [47]. It turns out to be a spatial average of the fluid temperature field $T(\mathbf{r})$ weighted by the local energy dissipation $\phi(\omega, \mathbf{r})$ due to the particle motion [48]. The energy spectrum of the thermal noise thus becomes colored due to the long-range (hydro)dynamical interactions between the particle and the fluid volumes kept at different temperatures. In practice, this means that the particle velocity and position appear to thermalize at different effective temperatures

$$\frac{1}{2}m\langle V^2 \rangle = \frac{1}{2}k_B T^V, \quad \frac{1}{2}\omega_0^2 m \langle X^2 \rangle = \frac{1}{2}k_B T^X, \quad (1.1)$$

which are selected from the spectrum $\overline{\mathcal{T}}(\omega)$ by the respective relaxation rates. The resulting theory thus appears as a promising paradigm for non-Markovian fluctuations caused by a nonequilibrium environment, such as glassy and living matter. The resulting theory thus appears as a promising paradigm for non-Markovian fluctuations caused by a nonequilibrium environment, such as glassy and living matter.

Then, rather than being after new principles, we content ourself with surveying cornerstone results of equilibrium statistical mechanics, i.e. the energy equipartition, virial theorem and the mechanical equation of state. In Chapter 3, we find useful generalizations for stationary Markovian systems driven by non-conservative forces f_i and simultaneously in contact with multiple heat reservoirs at temperature T_i , which feature the heat flux \dot{Q}_i into the baths over the damping time $1/\gamma_i$ on the same footing with thermodynamic variables [49],

$$\left\langle \frac{p_i^2}{m_i} \right\rangle = \left\langle q_i \left(\frac{\partial \mathcal{H}}{\partial q_i} - f_i \right) \right\rangle = k_B T_i + \frac{\dot{Q}_i}{\gamma_i}. \quad (1.2)$$

These novel relations are applied to some prototypical model systems [50, 51]: namely, heat conducting lattices, whose inhomogeneous energy distribution between the normal modes is characterized in terms of the driving and boundary conditions; suspensions of self-propelled particles [30], for which we confirm the pressure equation to be in general dependent on the confining forces—and not just on bulk properties.

In Chapter 4, we move into linear response theory of nonequilibrium states. We adopt a path integral approach, in which perturbations are viewed in the functional space of trajectories [52]. We extend the method to stochastic perturbations corresponding to temperature variations of the system's heat baths [49, 53]. In analogy to deterministic perturbations, we find that the thermal response of a generic observable \mathcal{O} ,

$$R_{\mathcal{O}}(t, t') = \frac{1}{2} \left\langle \mathcal{O}(t) \dot{S}(t') \right\rangle - \left\langle \mathcal{O}(t) \dot{K}(t') \right\rangle, \quad (1.3)$$

involves unperturbed correlations not solely determined by the entropy flux \dot{S} produced by the perturbation (as it is in equilibrium), but also by dynamical aspects \dot{K} that are non-dissipative, i.e. symmetric under time inversion. The utility of the theory is twofold. On the one hand, it allows one to extract thermal susceptibilities, such as heat capacity and thermal expansivity—key quantities in the construction of a general thermodynamic theory—from unperturbed correlation function. This is shown through simple numerical examples of heat conducting lattices, and experiments involving an RC circuit with components maintained at different temperatures and hydrodynamically interacting colloids under random driving [54, 55]. On the other hand, the theory can be used to consistently coarse-grain weakly-coupled systems when interactions between

them can be viewed as small mutual perturbations. By means of this approach we derive the generalized Langevin equation for a system of probe particles in contact with a driven environment, such as a suspension of self-propelled or sheared particle, whose dynamics is subsumed into dissipative and noisy forces breaking the fluctuation-dissipation theorem, and effective interactions not satisfying the action-reaction law [56].

Finally, in Chapter 4 we make an excursion into the topic of fluctuation theorems [12, 18], which are symmetry relations holding in irreversible processes for the statistics of thermodynamic quantities, such as entropy production and currents. Studying two different realizations (in computer simulations and experiments) of a laser-heated self-thermophoretic Brownian particle, we give empirical evidences of their applicability even though their validity is not *a priori* guaranteed [57]—as the solvent itself is out of equilibrium and the driving is inherently random. Moreover, we look for possible generalization to observables that are symmetric under time reversal—thus unconventional ones, in this context. For diffusion, processes we find that the phase space contraction rate (i.e. the sum of the Lyapunov exponents, giving the system’s sensitivity to perturbations) satisfies an integral fluctuation theorem [58] which parallels an earlier version for deterministic systems [59]. Also, we propose to extend such concepts to jump processes as well. Hence, we unravel formal and conceptual similarities between stochastic and deterministic systems, and highlight the possibility to obtain fluctuation relations for physical quantities not necessarily related to irreversibility.

Chapter 2

Brownian motion in a temperature gradient

Starting from the seminal work of Einstein [60], Brownian motion has become a milestone in the statistical theory of equilibrium fluctuations. It has never since ceased to attract attention and its laws have been recognized to pertain not exclusively to the realm of physics, but also to chemistry, biology, and even economics [61]. These laws, nowadays grounded in the theory of stochastic processes [62], have become a universal toolbox to describe randomness in science. Hence, Brownian motion, which originally referred to the thermal fluctuations of some mesoscopic particles in contact with a bath of smaller particles, generalizes to any slow degrees of freedom in contact with very many fast ones—the so-called “gross variables”, first appearing in [63]. The scale separation is the essential feature that allows for some coarse-graining of (otherwise intractable) many-body systems. A convenient approach to formalize this notion is via the generalized Langevin equation (GLE), that casts the effect of the dismissed degrees of freedom in the form of systematic dissipation and random fluctuations [64]:

$$m\dot{V}(t) = - \int_{-\infty}^t dt' \zeta(t-t')V(t') - \partial_x \mathcal{H}(X, V) + \xi(t). \quad (2.1)$$

Here V denotes the mesoscopic degree of freedom undergoing Brownian motion, such as the velocity of a suspended colloid acted on by the solvent friction $-\int_{-\infty}^t dt' \zeta(t-t')V(t')$ and the thermal noise ξ . If the bath is in thermal equilibrium, the process generated by (2.1) should reach equilibrium for long times, too. This is realized assigning the noise ξ a Gaussian weight that satisfies a *fluctuation-dissipation theorem*¹ (FDT)

$$\langle \xi(t)\xi(t') \rangle = k_B T \zeta(t-t'), \quad (2.2)$$

which equates the spontaneous correlations and the response² of the bath solely via its thermal energy $k_B T$ [65]. Equation (2.2)—an example of Kubo formula discussed in Chapter 4—is a formal statement of the Onsager regression hypothesis that “the average regression of fluctuations will obey the same laws as the corresponding macroscopic irreversible process” [66]. If only (conservative) forces deriving from a Hamiltonian

¹Of the *second kind*. One should be aware of its distinction from the FDT of the *first kind*, which involves the correlation $\langle V(t)V(0) \rangle$ and the (symmetrized) response $R_V(t)$ of the Brownian degree of freedom V , namely, $\langle V(t)V(0) \rangle = k_B T R_V(t)$ ($t > 0$). The former implies the latter if only conservative forces are added in (2.1). In practice, the degrees of freedom which satisfy an FDT act as a good thermal bath when coupled to other ones.

²To be precise, $\zeta(t) = \zeta(|t|)$ is the time-symmetric part of the response function.

$\mathcal{H}(X, V)$ are present in (2.1), the FDT (2.2) suffices to ensure that both $V \equiv \dot{X}$ and the conjugated position X relax to the equilibrium probability distribution

$$\rho(X, V) \propto e^{-\mathcal{H}(X, V)/k_B T}. \quad (2.3)$$

Also, as a consequence of (2.2) the static correlations induced by the GLE conform to the equipartition theorem [65]. For the emblematic case of a quadratic energy function $\mathcal{H} = \frac{1}{2}mV^2 + \frac{1}{2}\omega_0^2 mX^2$, it reads [67]

$$\frac{1}{2}m\langle V^2 \rangle = \frac{1}{2}\omega_0^2 m\langle X^2 \rangle = \frac{1}{2}k_B T, \quad (2.4)$$

and thus indicates a “fair” distribution of thermal energy between all degrees of freedom. At the level of trajectories, thermal equilibrium, i.e. the absence of probability currents, is manifest in the form of *detailed balance* [62]. This—made possible by (2.2) and the presence of conservative forces only—corresponds to the equality of forward and backward transition probabilities³ between two states with energy difference $\Delta H = \mathcal{H}(X_t, V_t) - \mathcal{H}(X_0, V_0)$,

$$P[X_t, V_t | X_0, V_0] = P[X_0, -V_0 | X_t, -V_t] e^{-\Delta H / (k_B T)}. \quad (2.5)$$

Because the two states may be seen as the initial and final points of a trajectory and its time-inverse, detailed balance corresponds to time reversibility of the stochastic process generated by (2.1).

Statistical arguments are not enough to yield a close form for (2.1), though. The friction $\zeta(t)$, being dynamical in nature, cannot be fixed by equilibrium statistical mechanics and its functional form needs to be worked out within an explicit coarse-graining procedure [68–70]. Typically, one resorts to (fluctuating) hydrodynamics theories [71, 72] that separate the wildly chaotic motion of the very many microscopic degrees of freedom from the more tractable dynamics of a few slow conserved fields, which contribute the memory effects contained in $\zeta(t)$. The latter are negligible only if there exists an *additional* strong timescale separation between the hydrodynamic fields and the Brownian variables, in which case $\zeta(t) \sim \delta(t)$, so that (2.1) boils down to a Markovian (i.e. memoryless) Langevin equation [73].

The Langevin theory remains valid even when the Brownian degrees of freedom are externally driven out of equilibrium as long as the source of nonequilibrium does not appreciably affect the bath: namely, when some non-potential force f is included in (2.1), or the Hamiltonian is endowed with a time-dependent parameter $\lambda(t)$, but (2.2) persists as is. The FDT then implies that (2.5) is replaced by *local* (or *generalized detailed balance* [74–77]),

$$P[X_t, V_t | X_0, V_0] = P[X_0, -V_0 | X_t, -V_t] e^{Q / (k_B T)}, \quad (2.6)$$

which quantifies the irreversibility of transitions between two states in terms of the corresponding heat flux into the thermal bath Q , over the bath temperature, i.e. the entropy flow $S = Q / (k_B T)$. It is the concept of a Brownian scale separation, as embodied in the GLE, that allows to univocally define thermodynamic quantities, like heat and entropy, at the mesoscopic scale. Indeed, the heat rate \dot{Q} into the bath is read off from the GLE as minus the rate of work done on the system by the bath forces [78],

$$\dot{Q} = - \left(\xi(t) - \int_{-\infty}^t dt' \zeta(t-t') V(t') \right) V(t) = -\dot{\mathcal{H}} + \dot{W}, \quad (2.7)$$

³The probability to move from, say, state x to state y is the product of the conditional probability $P[x|y]$ times the probability distribution $\rho(y)$.

and thus splits into the internal energy variation and the work rate⁴ on the system $\dot{W} \equiv fV + \partial_\lambda \mathcal{H}\dot{\lambda}$. Starting from these definitions, one can develop a framework of stochastic thermodynamics that plays a central role in describing conditions far from equilibrium, even when measurement and feedback are included [79], and in studying nonequilibrium fluctuation relations [18].

In contrast, none of the above symmetry properties generally survives on the Brownian scale if the bath itself is driven out of equilibrium. In soft matter physics one may think of granular, glassy, or active-particle suspensions, sheared and nonisothermal fluids, as typical nonequilibrium baths where one (ore more) Brownian particles are suspended [80–85]. It is certainly of great interest to establish a self-contained coarse-grained description for the colloid(s) in such situations. Yet, the equilibrium arguments invoked above in the construction of the GLE, are not any more applicable. So the reduced stochastic description must be found by other means, integrating out the dynamics of the nonequilibrium bath.

In our work [46, 48] we focus on the Brownian motion of a single colloid in a simple fluid subjected to a temperature gradient. The latter can be imposed by thermostats maintaing different temperatures at the boundaries or generated by the particle itself as a consequence of direct heating. This is indeed a very common situations in optical (tracking and trapping) techniques, which intentionally exploit heating or cause it as a side effect [86]. The resulting *hot Brownian motion* serves as a prototypical example to understand the main implications of a nonequilibrium bath. Building on the fluctuating hydrodynamics of the solvent [87], and its coupling to the hot particle, we derived the GLE (2.1) for the motion of the hot particle alone. In order to obtain a mesoscopic model essentially independent of molecular details we cannot renounce completely to take advantage of equilibrium concepts. We assume that the fluid, despite being globally far from equilibrium, is agitated by fluctuations satisfying a local FDT in which the inhomogeneous temperature field $T(\mathbf{r})$ enters. Hence, in contrast to standard Brownian dynamics, we do not require a direct buffering of the colloidal particle by some equilibrium thermal reservoir but only an indirect one, mediated by the nonequilibrium hydrodynamic fields. In [46] we demonstrate that typical experimental conditions comply with this assumption and derive the fluctuating hydrodynamics adequate for a Brownian particle suspended in solvents with moderate temperature gradients. Integrating out the solvent's superfluous degrees of freedom yields a remarkable generalization of the FDT (2.2) which was previously suggested to govern the linear response of glasses and slowly driven systems [47]. Its Fourier representation,

$$\langle \xi(\omega)\xi(\omega') \rangle = k_B \mathcal{T}(\omega)\zeta(\omega)\delta(\omega + \omega'), \quad (2.8)$$

is most convenient to show that a frequency-dependent noise temperature $\mathcal{T}(\omega)$ replaces the constant temperature of the equilibrium FDT (2.2). It turns out to be a spatial overage of the fluid temperature field $T(\mathbf{r})$ weighted by the local energy dissipation $\phi(\omega, \mathbf{r})$ due to the particle motion,

$$\mathcal{T}(\omega) = \frac{\int d\mathbf{r} T(\mathbf{r})\phi(\mathbf{r}, \omega)}{\int d\mathbf{r} \phi(\mathbf{r}, \omega)}. \quad (2.9)$$

The energy spectrum of the thermal noise thus becomes colored⁵ due to the long-range (hydro)dynamical interactions between the particle and the fluid volumes kept at different temperatures. Since ϕ is the fluid response upon particle displacements, the

⁴Comparing (2.5) with (2.6), the work W is seen to express the breaking of time reversibility.

⁵In a way reminiscent of the equilibrium *quantum* FDT [88].

noise temperature is not a property of the solvent or the particle, alone, but characterizes their mutual coupling. For arbitrary temperature gradients and particle shapes, \mathcal{T} is a tensor (since ϕ is), which reflects that hydrodynamic modes may carry different amounts of thermal energy along different spatial directions. Loosely speaking, this defies Maxwell's colloquial description of the zeroth law of thermodynamics, namely, all heat is of the same kind [89].

As a result, if we think of the Brownian particle as a thermometer operating far from equilibrium, its reading will depend on its orientation, shape, surface properties, as well as the variables being observed. In practice, this means that velocity and position (of a harmonically trapped particle) appear to thermalize at different effective temperatures

$$\frac{1}{2}m\langle V^2 \rangle = \frac{1}{2}k_B T^V, \quad \frac{1}{2}\omega_0^2 m \langle X^2 \rangle = \frac{1}{2}k_B T^X, \quad (2.10)$$

which are selected from the spectrum $\mathcal{T}(\omega)$ by the respective relaxation rates. One can turn this property to good account. A dense Brownian particle (is only weakly damped by the solvent and thus) can be endowed with a frequency filter peaked at ω_0 . Thereby, by varying the trap stiffness $m\omega_0^2$ it is turned into a genuine thermo(spectro)meter that measures only the resonant mode $\mathcal{T}(\omega_0)$ [90],

$$\frac{1}{2}m\langle V^2 \rangle = \frac{1}{2}\omega_0^2 m \langle X^2 \rangle = \frac{1}{2}k_B \mathcal{T}(\omega_0). \quad (2.11)$$

Differently from many previous approaches [91], these results are not postulated, but analytically derived. Therefore, they provide an independent testbed for rigorously analyzing the scope of the notion of effective temperatures, far from equilibrium.

Nonisothermal fluctuating hydrodynamics and Brownian motionG. Falasco^{1,2,*} and K. Kroy^{1,†}¹*Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, D-04009 Leipzig, Germany*²*Max Planck Institute for Mathematics in the Sciences, Inselstr. 22, 04103 Leipzig, Germany*

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The classical theory of Brownian dynamics follows from coarse graining the underlying linearized fluctuating hydrodynamics of the solvent. We extend this procedure to globally nonisothermal conditions, requiring only a local thermal equilibration of the solvent. Starting from the conservation laws, we establish the stochastic equations of motion for the fluid momentum fluctuations in the presence of a suspended Brownian particle. These are then contracted to the nonisothermal generalized Langevin description of the suspended particle alone, for which the coupling to stochastic temperature fluctuations is found to be negligible under typical experimental conditions.

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The microscopic equations of motion for strongly interacting many-body systems are, in general, intractable. A notable exception is provided by systems exhibiting a scale separation that allows for major simplifications of these equations, making them practically (and not only formally) useful in a wide range of experimental and technological applications. Of particular relevance is the so-called Brownian motion of a reduced number of slow degrees of freedom, for which the many fast degrees of freedom provide an effective background noise. As Einstein realized early on [1], the crucial simplification arises from the assumption that the microscopic and Brownian degrees of freedom are in thermal equilibrium, which allows for a universal characterization of the noise dynamics without explicit microscopic calculations. The corresponding theory of isothermal Brownian motion is by now firmly established and usually additionally exploits the fact that the mesoscopic degrees of freedom mediating between the Brownian scale and the microscopic noise degrees of freedom admit a coarse-grained hydrodynamic description, without loss of generality. In particular, starting with early work by Zwanzig [2], several papers have explicitly derived (generalized) Langevin equations describing Brownian motion as a contraction of the more detailed description of a fluid governed by linear fluctuating hydrodynamics [3–5]. Among the major outcomes of this inquiry there is the explanation of the long-time tails in the Brownian velocity autocorrelation function [6,7] and the robustness of the fluctuation-dissipation theorem against variations of microscopic details and even hydrodynamic specifications, such as the (in)compressibility of the solvent [8,9] or its (no-)slip boundary condition at the Brownian particle surface [10]. The necessary nanotechnological tools to conduct quantitative experimental tests of these ground-breaking theoretical developments have only become available very recently [11–13] and vindicated the central theoretical premise, i.e., the assumption of an underlying isothermal fluctuating solvent hydrodynamics, with impressive precision.

Conversely, very little is known about Brownian motion in nonequilibrium solvents where the validity of a Langevin description is not *a priori* ensured and standard recipes to leapfrog the microscopic dynamics using results from equilibrium statistical mechanics, such as energy equipartition, are not available. Yet microscale and nanoscale motion under nonequilibrium (and in particular nonisothermal) conditions are becoming increasingly relevant for innovative experimental and nanotechnological applications [14–16].

Linear fluctuating hydrodynamics, originally introduced by Landau and Lifshitz to describe density, momentum, and energy fluctuations of a fluid in a global equilibrium state [17], was later extended to nonequilibrium conditions, e.g., when a temperature gradient is present [18–21]. The efficacy of this nonequilibrium theory in describing fluid fluctuations is testified by the equivalence of its predictions to those of kinetic theory [22]—within its range of validity, i.e., for dilute gases—and mode-coupling theory [22–24] and by the good agreement with light-scattering experiments; see Ref. [25] for a review. In view of this success, one may expect the theory to be as effective in deriving reduced descriptions of the Brownian dynamics in nonisothermal solvents as in the equilibrium case.

The aim of the present work is twofold: first, to establish the fluctuating hydrodynamic equations of motion for a nonisothermal solvent, and second, to derive the coarse-grained description pertaining to a Brownian particle suspended therein. Section II develops the fluctuating hydrodynamic equations suitable for addressing the Brownian motion of a submicron-sized particle in a simple nonisothermal fluid. More precisely, the analysis of Sec. II shows that the coupling between momentum, temperature, and density gives rise to contributions that are at most proportional to $\epsilon_1 \equiv \Delta T \alpha_p$, where ΔT is the characteristic temperature variation in the system and α_p is the isobaric thermal expansion coefficient of the solvent. To get a feeling for the numbers involved, consider the paradigmatic example of a hot nanoparticle of radius $R \lesssim 100$ nm in water [26]. The temperature variations will usually be bounded by $\Delta T \lesssim 10^2$ K, so $\alpha_p \lesssim 10^{-3}$ K⁻¹ and it is safe to assume that $\epsilon_1 \ll 1$. To leading order, one can thus consider momentum and temperature fluctuations to be independent and the fluid density to be constant. Based on these findings, we construct the reduced description for the nonequilibrium dynamics of the immersed Brownian

*gianmaria.falasco@itp.uni-leipzig.de

†klaus.kroy@uni-leipzig.de

particle by eliminating the dynamical equations for the solvent fields, in Sec. III. The particle position \mathbf{R} turns out to evolve according to a generalized Langevin equation with long-term memory, whose zero-mean Gaussian noise satisfies a generalized fluctuation-dissipation theorem with a tensorial frequency-dependent energy spectrum $k_B \mathcal{T}_{ij}(\mathbf{R}, \omega)$ that implicitly reflects the lack of homogeneity and isotropy in the fluid. In Sec. IV we apply our theory to a simple yet paradigmatic example, namely, a spherical particle in a linear temperature field. Neglecting the temperature dependence of the fluid viscosity, we obtain the appropriate Langevin equation, showing that the noise temperature \mathcal{T}_{ij} reduces to the local fluid temperature, as usually postulated [27,28]. We also recall how such inhomogeneous noise translates into a thermodiffusion flux in the long-time limit and point out its relation to the thermophoresis observed in experiments with colloidal suspensions. Finally, in Sec. V, we summarize our results, leaving a more thorough discussion of the consequences on the level of the coarse-grained Langevin dynamics to Ref. [29].

II. FLUCTUATING HYDRODYNAMICS

The starting point for the following discussion is the deterministic hydrodynamic equations describing the conservation of mass, momentum, and energy in a compressible Newtonian fluid in local thermal equilibrium, which occupies the volume \mathcal{V} around a suspended Brownian particle of arbitrary shape. Expressing energy in terms of the fields T (local temperature) and p (local pressure) by means of the local-equilibrium version of the first law, we have [25,30]

$$\frac{d\varrho}{dt} = -\varrho \nabla \cdot \mathbf{v}, \quad (1a)$$

$$\varrho \frac{d\mathbf{v}}{dt} = -\nabla p + \nabla \cdot \mathbf{\Gamma} - \varrho g \hat{\mathbf{z}}, \quad (1b)$$

$$\varrho c_p \frac{dT}{dt} = -\nabla \cdot \mathbf{Q} - \left(\frac{\partial \varrho}{\partial T} \right)_p \frac{T}{\varrho} \frac{dp}{dt}, \quad (1c)$$

where ϱ is the mass density, \mathbf{v} the velocity, $\mathbf{\Gamma}$ the deviatoric stress tensor, \mathbf{Q} the heat flux, and c_p the specific heat capacity at constant pressure. The gravity force ϱg is directed along the negative z axis. We defined the total derivative $\frac{d}{dt} \equiv \partial_t + \mathbf{v} \cdot \nabla$ to simplify the notation and note that, in Eq. (1c), the temperature variations caused by the viscous heating arising from the fluid motion have been discarded as second order in the fluxes and therefore are negligible in comparison with \mathbf{Q} . The constitutive relations for the deviatoric stress tensor and the heat flux read

$$\mathbf{\Gamma} = \eta[\nabla \mathbf{v} + (\nabla \mathbf{v})^T] + \eta_b(\nabla \cdot \mathbf{v})\mathbf{1}, \quad (2)$$

$$\mathbf{Q} = -\kappa \nabla T, \quad (3)$$

where η , η_b , and κ are the dynamical shear and bulk viscosities and the heat conductivity, respectively. We also introduce the kinematic viscosity $\nu = \eta/\varrho$ and the heat diffusivity $a_T = \kappa/\varrho c_p$ (the diffusion coefficients of momentum and heat), for later convenience. We note that, at this stage, all transport coefficients can be thought of as spatially varying functions that would have to be specified, together with a material

law $\varrho(p, T)$, to close the system of equations. Having highly incompressible solvents such as water in mind, we simplify the following discussion by demanding perfect incompressibility, from the outset. Thereby, we forgo the opportunity to faithfully discuss very fast processes (faster than the time a sound wave needs to travel across a distance of about the particle size). By moreover neglecting a possible temperature dependence of the expansion coefficient α_p , which is again justifiable for water, the deterministic equations of motion for the solvent are closed by the simple material relation

$$\varrho(\mathbf{r}, t) = \varrho_0[1 - \alpha_p(T(\mathbf{r}, t) - T_0)], \quad (4)$$

where $\varrho_0 \equiv \varrho(T_0)$ is the density corresponding to the reference ambient temperature T_0 and terms of $O(\epsilon_1^2)$ are neglected.

The boundary condition associated with Eq. (1b), which accounts for the momentum exchange with the suspended Brownian particle, is the no-slip condition at the particle surface \mathcal{S} , i.e.,

$$\mathbf{v}(\mathbf{r}, t) = \langle \mathbf{V}(t) \rangle + \langle \mathbf{\Omega}(t) \rangle \times \mathbf{r} \quad \text{on } \mathcal{S}, \quad (5)$$

where $\langle \mathbf{V} \rangle$ and $\langle \mathbf{\Omega} \rangle$ are the deterministic translational and angular velocities of the particle, respectively.¹ The boundary conditions for Eq. (1c), which describe the heat sources maintaining the inhomogeneous temperature field, as well as the particle's equations of motion, are for the moment irrelevant.

Equations (1) provide the basis for describing the deterministic evolution of the coarse-grained nonequilibrium state of the fluid. Fluctuations about this average state can be incorporated by adding stochastic terms to the stress tensor and the heat flux by substituting $\mathbf{\Gamma} \rightarrow \delta \mathbf{\Gamma} + \boldsymbol{\tau}$ and $\mathbf{Q} \rightarrow \delta \mathbf{Q} + \mathbf{J}$, in order to represent the random exchange of momentum and energy between the hydrodynamic and the omitted microscopic degrees of freedom [17,25]. As a consequence, the hydrodynamic fields also acquire stochastic contributions according to $\mathbf{v} \rightarrow \mathbf{v} + \delta \mathbf{v}$, $p \rightarrow p + \delta p$, and $T \rightarrow T + \delta T$. Consistency with the local-equilibrium hypothesis sets two constraints. First, the probability densities of $\boldsymbol{\tau}$ and \mathbf{J} must be Gaussian with mean zero and their variance obeying the local fluctuation-dissipation theorem governed by the deterministic local values of the temperature field. Second, the stochastic equations obeyed by the fluctuating fields should be linearized, since nonlinear contributions to the random fluxes are small by construction. Namely, we wish to remain within the domain of validity of nonequilibrium thermodynamics, in which the dissipative fluxes are linear functions of the gradients of the hydrodynamic fields. Thus, nonlinearities may only arise due to the functional dependences of the transport coefficients [31,32]. In typical colloidal experiments, only the viscosity presents a meaningful temperature dependence, which we retain *a priori*, and eventually is shown to be negligible.

We proceed as follows. First, we identify further subleading-order terms in the deterministic hydrodynamic equations, which we simplify accordingly. We then insert the random contributions to the stress tensor and the heat flux to

¹The time dependence of \mathcal{S} will always be neglected in the following. This amounts to moving to the particle frame and dropping the advection terms.

obtain the corresponding stochastic equations of motion. Our analysis closely follows the one used in the Rayleigh-Bénard problem leading to the linearized fluctuating Boussinesq equations [25]. However, an important difference concerns the characteristic length scale R in the two problems. Namely, in our system the relevant length scale is set by the particle size, which we assume to be at least several nanometers and less than a micron, typically on the order of $R \simeq 10^{-7}$ m. On this scale, advection is much less effective than diffusion in spreading momentum and heat in the fluid. The relative magnitude of advection and diffusion terms in Eqs. (1b) and (1c) is estimated as

$$O\left(\frac{|\mathbf{v} \cdot \nabla \mathbf{v}|}{|\mathbf{v} \nabla^2 \mathbf{v}|}\right) \simeq \text{Re}, \quad O\left(\frac{|\mathbf{v} \cdot \nabla T|}{|a_T \nabla^2 T|}\right) \simeq \text{Pe}, \quad (6)$$

where $\text{Re} \equiv vR/\nu$ and $\text{Pe} \equiv \text{Re}v/a_T$ are the Reynolds and Péclet numbers associated with the particle's motion, respectively. To remain consistent with the local equilibrium assumption, the characteristic deterministic particle velocity (that sets the order of magnitude of the fluid velocity \mathbf{v}) must remain bounded by the thermal velocity $V_{\text{th}} \sim \sqrt{k_B T / \rho_p R^3}$, where R and ρ_p denote the radius and mass density of the particle, respectively. In practice, deterministic particle velocities are usually much smaller. With $\rho_p \simeq \rho_0$ this translates to $\text{Re} \simeq 10^{-3}$ and $\text{Pe} \simeq 10^{-2}$, which implies that advection can be neglected, so the total derivative d/dt can be replaced by the partial derivative ∂_t when acting on \mathbf{v} and T , in the above equations.

Under these conditions, after substituting Eq. (4) into the balance equations (1a)–(1c) the deterministic equations of motion for the solvent degrees of freedom become

$$\alpha_p \partial_t T = [1 - \alpha_p(T - T_0)] \nabla \cdot \mathbf{v}, \quad (7a)$$

$$\rho_0 [1 - \alpha_p(T - T_0)] \partial_t \mathbf{v} = -\nabla p + \nabla \cdot \mathbf{\Gamma} - \rho_0 [1 - \alpha_p(T - T_0)] g \hat{\mathbf{z}}, \quad (7b)$$

$$\rho_0 c_p [1 - \alpha_p(T - T_0)] \partial_t T = -\nabla \cdot \mathbf{Q} + \frac{\alpha_p T}{1 - \alpha_p(T - T_0)} \frac{dp}{dt}. \quad (7c)$$

Notice that, in general, momentum and temperature do not evolve independently. In order to understand the relative importance of the different terms determining such coupling we switch to dimensionless variables

$$\tilde{\mathbf{r}} R \equiv \mathbf{r}, \quad \tilde{t} \frac{R^2}{a_T} \equiv t, \quad \tilde{\mathbf{v}} \frac{a_T}{R} \equiv \mathbf{v}, \quad (8)$$

$$\tilde{T} \Delta T \equiv T, \quad \tilde{\mathbf{\Gamma}} \frac{\rho_0 a_T^2}{R^2} \equiv \mathbf{\Gamma}, \quad \tilde{\mathbf{Q}} \frac{\rho_0 c_p a_T \Delta T}{R} \equiv \mathbf{Q}. \quad (9)$$

For simplicity we have taken a_T and c_p constant here. Equations (7) in dimensionless form are

$$\epsilon_1 \partial_t \tilde{T} = [1 - \epsilon_1(\tilde{T} - \tilde{T}_0)] \tilde{\nabla} \cdot \tilde{\mathbf{v}}, \quad (10a)$$

$$[1 - \epsilon_1(\tilde{T} - \tilde{T}_0)] \partial_t \tilde{\mathbf{v}} = -\tilde{\nabla}(\tilde{p} + \epsilon_2 \tilde{z}) + \tilde{\nabla} \cdot \tilde{\mathbf{\Gamma}} + \epsilon_1 \epsilon_2 \hat{\mathbf{z}}, \quad (10b)$$

$$[1 - \epsilon_1(\tilde{T} - \tilde{T}_0)] \partial_t \tilde{T} = -\tilde{\nabla} \cdot \tilde{\mathbf{Q}} + \frac{\epsilon_3 \tilde{T}}{1 - \epsilon_1(\tilde{T} - \tilde{T}_0)} \frac{d\tilde{p}}{d\tilde{t}}. \quad (10c)$$

The magnitude of the various terms can be estimated by checking the physical values of the dimensionless parameters $\epsilon_1 \equiv \alpha_p \Delta T$, $\epsilon_2 \equiv R^3 g / a_T^2$, and $\epsilon_3 \equiv \alpha_p a_T^2 / c_p R^2$, which control the relative magnitude of temperature-induced inhomogeneities in density, buoyancy, and pressure-driven heat fluxes, respectively. Taking R and ΔT as above, we obtain for water around standard conditions $\epsilon_1 \simeq 10^{-2}$, $\epsilon_2 \simeq 10^{-6}$, and $\epsilon_3 \simeq 10^{-7}$. This implies that the limit $\epsilon_1, \epsilon_2, \epsilon_3 \rightarrow 0$ reproduces the leading behavior of Eq. (10), while perturbative corrections should follow by expanding the hydrodynamic fields in series of these small parameters. To leading order, Eq. (10) then read

$$\tilde{\nabla} \cdot \tilde{\mathbf{v}} = 0, \quad (11a)$$

$$\partial_t \tilde{\mathbf{v}} = -\tilde{\nabla} \tilde{p} + \tilde{\nabla} \cdot \tilde{\mathbf{\Gamma}}, \quad (11b)$$

$$\partial_t \tilde{T} = -\tilde{\nabla} \cdot \tilde{\mathbf{Q}}. \quad (11c)$$

The condition (11a) of a divergence-free velocity field means that the fluid density can be treated as a constant. Restoring the physical dimensions, we obtain our final set of deterministic equations

$$\nabla \cdot \mathbf{v}(\mathbf{r}, t) = 0, \quad (12a)$$

$$\rho_0 \partial_t \mathbf{v}(\mathbf{r}, t) = -\nabla \cdot [p(\mathbf{r}, t) \mathbf{1} - \mathbf{\Gamma}(\mathbf{r}, t)], \quad (12b)$$

$$\partial_t T(\mathbf{r}, t) = -a_T \nabla^2 T(\mathbf{r}, t), \quad (12c)$$

where the temperature dependence of the viscosity $\eta[T(\mathbf{r}, t)]$ in the deviatoric stress tensor $\mathbf{\Gamma}(\mathbf{r}, t)$ is retained.

Now we turn to fluctuations and introduce the random stress and heat flux into Eqs. (12b)–(12c). The resulting fluctuating fields obey the equations

$$\nabla \cdot \delta \mathbf{v}(\mathbf{r}, t) = 0, \quad (13a)$$

$$\rho_0 \partial_t \delta \mathbf{v}(\mathbf{r}, t) = -\nabla \cdot \{\delta p(\mathbf{r}, t) \mathbf{1} - \eta[T(\mathbf{r}, t)] [\nabla \delta \mathbf{v}(\mathbf{r}, t) + \nabla \delta \mathbf{v}(\mathbf{r}, t)^T]\} + \nabla \cdot \boldsymbol{\tau}(\mathbf{r}, t), \quad (13b)$$

$$\partial_t \delta T(\mathbf{r}, t) = -a_T \nabla^2 \delta T(\mathbf{r}, t) - \nabla \cdot \mathbf{J}(\mathbf{r}, t). \quad (13c)$$

Clearly, the boundary condition (5) becomes

$$\delta \mathbf{v}(\mathbf{r}, t) = \delta \mathbf{V}(t) + \delta \boldsymbol{\Omega}(t) \times \mathbf{r} \quad \text{on } \mathcal{S}, \quad (14)$$

where $\delta \mathbf{V}$ and $\delta \boldsymbol{\Omega}$ are the stochastic components of the particle velocities. The correlations of $\boldsymbol{\tau}$ and \mathbf{J} are prescribed by the local-equilibrium fluctuation-dissipation relations

$$\langle \tau_{ij}(\mathbf{r}, t) \tau_{kl}(\mathbf{r}', t') \rangle = 2\eta[T(\mathbf{r}, t)] k_B T(\mathbf{r}, t) \delta(\mathbf{r} - \mathbf{r}') \times \delta(t - t') (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}), \quad (15a)$$

$$\langle J_i(\mathbf{r}, t) J_j(\mathbf{r}', t') \rangle = 2a_T k_B T(\mathbf{r}, t)^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \delta_{ij}, \quad (15b)$$

$$\langle \tau_{ij}(\mathbf{r}, t) J_k(\mathbf{r}', t') \rangle = 0, \quad (15c)$$

containing only the deterministic part of the temperature field [25]. Consistency with the no-slip boundary condition requires that $\boldsymbol{\tau} = 0$ on S [4, 10].²

Notice that in going from Eq. (12b) to Eq. (13b), we have linearized the viscous stress. Indeed, direct insertion of fluctuations in Eq. (12b) would produce

$$\begin{aligned} & \eta[T + \delta T] \{ \nabla(\mathbf{v} + \delta\mathbf{v}) + [\nabla(\mathbf{v} + \delta\mathbf{v})]^T \} \\ & \simeq \left(\eta[T] + \frac{\partial\eta}{\partial T}[T]\delta T \right) [\nabla\mathbf{v} + (\nabla\mathbf{v})^T] \\ & + \eta[T][\nabla\delta\mathbf{v} + (\nabla\delta\mathbf{v})^T]. \end{aligned} \quad (16)$$

Here we have expanded the viscosity up to first order in δT and dropped the manifestly nonlinear fluctuation term proportional to $\delta T \nabla \delta \mathbf{v}$. Equation (13b) follows by neglecting the contribution due to temperature variations in the viscosity, which is justified by the observation

$$O\left(\frac{|(\partial\eta/\partial T)\delta T \nabla \mathbf{v}|}{|\eta \nabla \delta \mathbf{v}|}\right) \sim \frac{\Delta\eta}{\eta} \frac{\sqrt{\langle \delta T^2 \rangle}}{\Delta T} \frac{V_{\text{ex}}}{V_{\text{th}}} \ll 1. \quad (17)$$

While the typical relative viscosity variation $\Delta\eta/\eta$ is of the same order as the characteristic relative temperature variation $\Delta T/T_0$, in any coarse-graining volume consisting of N solvent molecules, the spontaneous nonequilibrium local temperature fluctuations $\sqrt{\langle \delta T^2 \rangle}$ are small compared to T and can be estimated to be of $O(1/N^{1/6})$ [33]. Moreover, the boundary conditions with the Brownian particle (5) and (14) fix the order of magnitude of the deterministic and fluctuating velocity fields to the typical particle velocity V_{ex} imposed by external forces and the particle thermal velocity V_{th} , respectively. As noted above, $V_{\text{ex}} \ll V_{\text{th}}$ is required to conform with the underlying local equilibrium assumption. In typical applications $V_{\text{ex}} \lesssim 10^{-6} \text{ m s}^{-1}$ is indeed substantially smaller than the thermal velocity $V_{\text{th}} \simeq 10^{-2} \text{ m s}^{-1}$.

We thus arrive at the important conclusion that momentum and temperature are decoupled up to corrections of $O(\epsilon_1)$ or smaller. The reason is that only the deterministic temperature $T(\mathbf{r}, t)$ appears in Eq. (13b), which is fully determined by Eq. (12c).

It is interesting now to go back to the starting point of the present analysis, i.e., the assumption of vanishing solvent compressibility $\kappa_T = 0$, which permits us to assume density variations to arise from temperature heterogeneities alone. A rough estimation of the relative density variation due to pressure variations can be obtained as follows. According to Eqs. (12a)–(12c), the fluid is divergence-free to leading order. The typical magnitude of (stationary) velocity and pressure variations can thus be approximated, employing the fundamental solution of the stationary Stokes equation, by $V_{\text{th}} \sim F/\eta R$ and $p_{\text{th}} \sim F/R^2$. Eliminating the thermal force F exerted by the fluid, we arrive at $p_{\text{th}} \sim \eta V_{\text{th}}/R \simeq 1 \text{ N m}^{-2}$. Thus for water we get

$$O\left(\frac{d\rho}{\rho}\bigg|_T\right) \simeq O(\kappa_T p_{\text{th}}) \sim 10^{-9}, \quad (18)$$

²Alternatively, one can drop the condition $\boldsymbol{\tau} = 0$ on S and include the random stress in the definition of the random force $\delta\mathbf{F}$ and torque $\delta\mathbf{T}$ on the particle. The two choices are mathematically equivalent.

which demonstrates the reliability of the assumption $\kappa_T = 0$ on time scales much longer than $R\sqrt{\kappa_T\rho_0} \simeq 10^{-10} \text{ s}$.

On the basis of Eqs. (12) and (13), in the next section we derive the generalized Langevin equation for the suspended Brownian particle and its associated noise spectrum.

III. DERIVATION OF THE PARTICLE'S GENERALIZED LANGEVIN EQUATION

We now focus on the nonequilibrium Brownian particle dynamics. The full state of the fluid-particle system is given in terms of the hydrodynamic fields and the particle coordinates, namely, the center-of-mass position $\mathbf{R}(t) = (\mathbf{X}(t), \mathbf{Y}(t), \mathbf{Z}(t))$ and the translational and rotational velocity $\mathbf{V}(t) = \langle \mathbf{V}(t) \rangle + \delta\mathbf{V}(t)$ and $\boldsymbol{\Omega}(t) = \langle \boldsymbol{\Omega}(t) \rangle + \delta\boldsymbol{\Omega}(t)$, respectively. The latter evolve by Newton's equations of motion

$$m\dot{\mathbf{V}} = \mathbf{F} + \delta\mathbf{F} + \mathbf{F}_{\text{ext}}, \quad (19a)$$

$$\mathbf{I} \cdot \dot{\boldsymbol{\Omega}} = \mathbf{T} + \delta\mathbf{T} + \mathbf{T}_{\text{ext}}, \quad (19b)$$

where m is the mass of the particle and \mathbf{I} its tensor of inertia. The deterministic force and torque exerted by the fluid are, respectively,

$$\mathbf{F}(t) = - \int_S \boldsymbol{\sigma}(\mathbf{r}, t) \cdot \mathbf{n}(\mathbf{r}) d^2r, \quad (20a)$$

$$\mathbf{T}(t) = - \int_S \mathbf{r} \times [\boldsymbol{\sigma}(\mathbf{r}, t) \cdot \mathbf{n}(\mathbf{r})] d^2r, \quad (20b)$$

where $\mathbf{n}(\mathbf{r})$ is the inner normal vector field of the particle surface S and

$$\boldsymbol{\sigma} = -p\mathbf{1} + \boldsymbol{\Gamma} \quad (21)$$

is the total stress tensor. Analogous definitions hold for the random force $\delta\mathbf{F}$ and torque $\delta\mathbf{T}$, replacing $\boldsymbol{\sigma}$ by $\delta\boldsymbol{\sigma}$. External forces $\mathbf{F}_{\text{ext}}(t)$ and torques $\mathbf{T}_{\text{ext}}(t)$ may also be present. The system of equations (12), (13), (19), and (20) entirely describes the evolution of the fluid and the Brownian particle. Our aim is to eliminate the equations for the hydrodynamic fields and reduce Eqs. (19) and (20) to a generalized Langevin equation for the particle variables only. Therefore, we rewrite Eq. (19) in the form

$$\mathbf{L} \cdot \dot{\mathbf{b}} = \mathbf{h} + \delta\mathbf{h} + \mathbf{f}_{\text{ext}}, \quad (22)$$

where we combine the translational and rotational velocities into the 6-vector $\mathbf{b} \equiv (\mathbf{V}, \boldsymbol{\Omega})$ and we define the generalized tensor of inertia

$$\mathbf{L} \equiv \begin{pmatrix} m\mathbf{1} & 0 \\ 0 & \mathbf{I} \end{pmatrix}$$

and the generalized forces

$$\mathbf{h} \equiv \begin{pmatrix} \mathbf{F} \\ \mathbf{T} \end{pmatrix}, \quad \delta\mathbf{h} \equiv \begin{pmatrix} \delta\mathbf{F} \\ \delta\mathbf{T} \end{pmatrix}, \quad \mathbf{f}_{\text{ext}} \equiv \begin{pmatrix} \mathbf{F}_{\text{ext}} \\ \mathbf{T}_{\text{ext}} \end{pmatrix}. \quad (23)$$

By Eqs. (12b), (12a), (5), and (14), $\mathbf{v}(\mathbf{r}, t)$ and $p(\mathbf{r}, t)$ are linear functionals of $\mathbf{b}(t')$ with $-\infty < t' < t$. Thus, in view of Eq. (20), the hydrodynamic forces necessarily contain a contribution that is a linear

functional of $\mathbf{b}(t')$ with $-\infty < t' < t$, i.e., we can write

$$\mathbf{h}(t) = - \int_{-\infty}^{\infty} \mathcal{Z}^+(\mathbf{R}, t - t') \cdot \langle \mathbf{b}(t') \rangle dt'. \quad (24)$$

Here $\mathcal{Z}^+(\mathbf{R}, t)$ is a 6×6 time-dependent causal friction tensor, which depends on the particle position owing to the nonconstant fluid viscosity. We omit this dependence in the following. The very same reasoning applies to $\delta\mathbf{h}$, but in addition, since (13b) is a nonhomogeneous equation due to the presence of the random stress $\boldsymbol{\tau}$, a term $\boldsymbol{\xi}(t)$ has to be included in order to account for contributions independent of the particle velocity. Hence $\delta\mathbf{h}$ consists of a friction term and a Langevin noise

$$\delta\mathbf{h}(t) = - \int_{-\infty}^{\infty} \mathcal{Z}^+(\mathbf{R}, t - t') \cdot \delta\mathbf{b}(t') dt' + \boldsymbol{\xi}(t). \quad (25)$$

In the subsequent derivation we will establish the statistics of the Langevin noise $\boldsymbol{\xi}(t)$ and relate it to the dissipative term $\mathbf{h}(t)$. The linearity of the problem suggests that one operate in frequency space. Given a generic function of time $g(t)$, we denote its Fourier transform by $g(\omega) = \int_{-\infty}^{\infty} g(t) e^{-i\omega t} dt$. The complex conjugate of $g(\omega)$ will be denoted by $g^*(\omega)$.

In Fourier space Newton's equation (22) reads

$$-i\omega\mathbf{L} \cdot \mathbf{b}(\omega) = -\mathcal{Z}^+(\omega) \cdot \mathbf{b}(\omega) + \boldsymbol{\xi}(\omega) + \mathbf{f}_{\text{ext}}(\omega), \quad (26)$$

where we used the Fourier-transformed equations (24) and (25),

$$\mathbf{h}(\omega) = -\mathcal{Z}^+(\omega) \cdot \langle \mathbf{b}(\omega) \rangle, \quad (27a)$$

$$\delta\mathbf{h}(\omega) = -\mathcal{Z}^+(\omega) \cdot \delta\mathbf{b}(\omega) + \boldsymbol{\xi}(\omega). \quad (27b)$$

Note that the deterministic part of the velocity vector $\langle \mathbf{b}(\omega) \rangle$ is set by the external force and thus can be chosen arbitrarily.

We are now in the position to evaluate the statistics of the Langevin noise $\boldsymbol{\xi}(\omega)$. We proceed in three steps. First, we derive an expression for (twice) the real part of the friction tensor defined by

$$\mathcal{Z}_{ij}(\omega) \equiv \mathcal{Z}_{ij}^+(\omega) + \mathcal{Z}_{ij}^{+*}(\omega). \quad (28)$$

To evaluate the components of the friction tensor we make use of the property $\mathcal{Z}_{ij}^+ = \mathcal{Z}_{ji}^+$, hinging only on the symmetry of the stress tensor $\sigma_{ij} = \sigma_{ji}$ [4]. We exploit the freedom of choosing the boundary condition (5) to select velocity vectors whose α th entry is the only nonzero one and denote them by ${}^\alpha b_i(\omega)$ (the superscript α will also be appended to the corresponding hydrodynamic fields). Second, we show that $\boldsymbol{\xi}(\omega)$ is a Gaussian variable with zero mean. Finally, we link the noise correlation tensor $\langle \xi_i(\omega) \xi_j^*(\omega) \rangle$ to the friction tensor (28).

We wish to find an expression in terms of the solution to Eq. (12b)—without formally solving the much more involved problem represented by the stochastic equations (13b)—for the quantity

$$\mathcal{Z}_{ij}(\omega) \langle {}^\alpha b_i(\omega) \rangle \langle {}^\beta b_j^*(\omega) \rangle = \mathcal{Z}_{\alpha\beta}(\omega) \langle b_\alpha(\omega) \rangle \langle b_\beta^*(\omega) \rangle, \quad (29)$$

where the equality holds by virtue of the choice of $\mathbf{b}(\omega)$. In Eq. (29) and in the following we apply the Einstein summation convention to latin indices only. Also, we suppress the function arguments where there is no risk of confusion. Equation (29) reads

$$\begin{aligned} \mathcal{Z}_{ij} \langle {}^\alpha b_i \rangle \langle {}^\beta b_j^* \rangle &\stackrel{(28)}{=} (\mathcal{Z}_{ij}^+ + \mathcal{Z}_{ij}^{+*}) \langle {}^\alpha b_i \rangle \langle {}^\beta b_j^* \rangle \stackrel{(27a)}{=} -\langle {}^\alpha h_i \rangle \langle {}^\beta b_j^* \rangle + \langle {}^\alpha b_i \rangle \langle {}^\beta h_j^* \rangle \\ &\stackrel{(20),(23)}{=} \langle {}^\beta V_i^* \rangle \int_S \alpha \sigma_{ij} n_j d^2 r + \langle {}^\beta \Omega_i^* \rangle \int_S [\mathbf{r} \times (\alpha \boldsymbol{\sigma} \cdot \mathbf{n})]_i d^2 r + \langle {}^\alpha V_i \rangle \int_S \beta \sigma_{ij}^* n_j d^2 r + \langle {}^\alpha \Omega_i \rangle \int_S [\mathbf{r} \times (\beta \boldsymbol{\sigma}^* \cdot \mathbf{n})]_i d^2 r \\ &= \int_S (\langle {}^\beta \mathbf{V}^* \rangle + \langle {}^\beta \boldsymbol{\Omega}^* \rangle \times \mathbf{r})_i \alpha \sigma_{ij} n_j d^2 r + \int_S (\langle {}^\alpha \mathbf{V} \rangle + \langle {}^\alpha \boldsymbol{\Omega} \rangle \times \mathbf{r})_i \beta \sigma_{ij}^* n_j d^2 r \\ &\stackrel{(5)}{=} \int_S \beta v_i^* \alpha \sigma_{ij} n_j d^2 r + \int_S \alpha v_i \beta \sigma_{ij}^* n_j d^2 r \\ &= \int_V \partial_j (\beta v_i^* \alpha \sigma_{ij}) d^3 r + \int_V \partial_j (\alpha v_i \beta \sigma_{ij}^*) d^3 r \\ &\stackrel{(12b)}{=} \int_V (\alpha \sigma_{ij} \partial_j \beta v_i^* + \beta \sigma_{ij}^* \partial_j \alpha v_i) + i\varrho\omega \int_V (\alpha v_i^* \beta v_i - \beta v_i^* \alpha v_i) d^3 r \\ &\stackrel{(12a)}{=} \int_V (\alpha \Gamma_{ij} \partial_j \beta v_i^* + \beta \Gamma_{ij}^* \partial_j \alpha v_i) d^3 r + i\varrho\omega \int_V (\alpha v_i^* \beta v_i - \beta v_i^* \alpha v_i) d^3 r \\ &= 2 \int_V \phi_{\alpha\beta} d^3 r - 2\varrho\omega \text{Im} \int_V \alpha v_i^* \beta v_i d^3 r, \end{aligned} \quad (30)$$

where in (30) we used the divergence theorem and in (31) we defined the generalized dissipation tensor

$$\phi_{\alpha\beta}(\mathbf{R}, \mathbf{r}, \omega) \equiv \eta(\mathbf{r}) [\partial_i \alpha v_j(\mathbf{r}, \omega) \partial_i \beta v_j^*(\mathbf{r}, \omega) + \partial_i \beta v_j(\mathbf{r}, \omega) \partial_j \alpha v_i^*(\mathbf{r}, \omega)] = \phi_{\beta\alpha}^*(\mathbf{R}, \mathbf{r}, \omega), \quad (32)$$

where the \mathbf{R} dependence of the hydrodynamic fields is not explicitly displayed. For general particle shapes and boundary conditions, it is obtained by solving the time-dependent deterministic Stokes equation (12b). For constant viscosity, the dynamical Oseen tensor [34], which is the Green's function of Eq. (12b), allows one to find the required solution. Equation (31) is valid

whatever the magnitude of ${}^\alpha b_i$ and ${}^\beta b_j^*$, in particular when they are unit vectors. With this choice we have

$$\mathcal{Z}_{\alpha\beta}(\mathbf{R}, \omega) = 2 \int_{\mathcal{V}} \phi_{\alpha\beta} d^3r - 2Q\omega \operatorname{Im} \int_{\mathcal{V}} {}^\alpha v_i^* {}^\beta v_i d^3r. \quad (33)$$

Since $\mathcal{Z}_{\alpha\beta}$ is real by definition, Eqs. (33) and (32) imply that $\phi_{\alpha\beta} = \phi_{\beta\alpha}$. Besides, Eq. (33) has to be invariant under exchange of α and β owing to the symmetry $\mathcal{Z}_{\alpha\beta} = \mathcal{Z}_{\beta\alpha}$. Therefore, one can eliminate the second term in Eq. (33) and obtain

$$\mathcal{Z}_{\alpha\beta}(\mathbf{R}, \omega) = 2 \int_{\mathcal{V}} \phi_{\alpha\beta}(\mathbf{R}, \mathbf{r}, \omega) d^3r. \quad (34)$$

Then we turn to the random force $\xi(\omega)$:

$$\begin{aligned} \xi_i \langle {}^\alpha b_i \rangle &\stackrel{(27b)}{=} (\delta h_i + \mathcal{Z}_{ij}^+ \delta b_j) \langle {}^\alpha b_i \rangle \stackrel{(27a)}{=} \delta h_i \langle {}^\alpha b_i \rangle - {}^\alpha h_j \delta b_j \\ &\stackrel{(20)}{=} -\langle {}^\alpha V_i \rangle \int_S \delta \sigma_{ij} n_j d^2r - \langle {}^\alpha \Omega_i \rangle \int_S [\mathbf{r} \times (\delta \boldsymbol{\sigma} \cdot \mathbf{n})]_i d^2r + \delta V_i \int_S {}^\alpha \sigma_{ij} n_j d^2r + \delta \Omega_i \int_S [\mathbf{r} \times ({}^\alpha \boldsymbol{\sigma} \cdot \mathbf{n})]_i d^2r \\ &= -\int_S (\langle {}^\alpha \mathbf{V} \rangle + \langle {}^\alpha \boldsymbol{\Omega} \rangle \times \mathbf{r})_i \delta \sigma_{ij} n_j d^2r + \int_S (\delta \mathbf{V} + \delta \boldsymbol{\Omega} \times \mathbf{r})_i {}^\alpha \sigma_{ij} n_j d^2r \\ &\stackrel{(5),(14)}{=} -\int_S {}^\alpha v_i \delta \sigma_{ij} n_j d^2r + \int_S \delta v_i {}^\alpha \sigma_{ij} n_j d^2r \\ &= -\int_{\mathcal{V}} \partial_j ({}^\alpha v_i \delta \sigma_{ij}) d^3r + \int_{\mathcal{V}} \partial_j (\delta v_i {}^\alpha \sigma_{ij}) d^3r \end{aligned} \quad (35)$$

$$\begin{aligned} &\stackrel{(12b),(13b)}{=} -\int_{\mathcal{V}} \delta \sigma_{ij} \partial_j {}^\alpha v_i d^3r + \int_{\mathcal{V}} {}^\alpha \sigma_{ij} \partial_j \delta v_i d^3r - \int_{\mathcal{V}} {}^\alpha v_i \partial_j \tau_{ij} d^3r \\ &\stackrel{(12a),(13a)}{=} -\int_{\mathcal{V}} {}^\alpha v_i \partial_j \tau_{ij} d^3r = \int_{\mathcal{V}} \tau_{ij} \partial_j {}^\alpha v_i d^3r. \end{aligned} \quad (36)$$

In (35) we made use of the divergence theorem and in (36) of the property $\delta \sigma_{ij} \partial_j {}^\alpha v_i = {}^\alpha \sigma_{ij} \partial_j \delta v_i$, which is a direct consequence of the symmetry of $\boldsymbol{\sigma}$. We thus have

$$\xi_i \langle {}^\alpha b_i \rangle = \xi_\alpha \langle b_\alpha \rangle = \int_{\mathcal{V}} \tau_{ij} \partial_j {}^\alpha v_i d^3r, \quad (37)$$

which shows that ξ is Gaussian with vanishing mean, being the integral of the deterministic quantity $\partial_j {}^\alpha v_i$ times the zero-mean Gaussian field $\boldsymbol{\tau}$. Hence, its correlation matrix suffices to specify the statistics completely. Using (37), we determine the noise correlation

$$\begin{aligned} \langle \xi_i(\omega) \xi_j^*(\omega') \rangle \langle {}^\alpha b_i(\omega) \rangle \langle {}^\beta b_j^*(\omega') \rangle &= \langle \xi_\alpha(\omega) \xi_\beta^*(\omega') \rangle \langle b_\alpha(\omega) \rangle \langle b_\beta^*(\omega') \rangle \\ &= \int_{\mathcal{V}} d^3r' \int_{\mathcal{V}} d^3r \partial_j {}^\alpha v_i(\mathbf{r}, \omega) \langle \tau_{ij}(\mathbf{r}, \omega) \tau_{kl}^*(\mathbf{r}', \omega') \rangle \partial_l {}^\beta v_k^*(\mathbf{r}', \omega') \end{aligned} \quad (38)$$

$$= 2k_B \delta(\omega - \omega') \int_{\mathcal{V}} \eta(\mathbf{r}) T(\mathbf{r}) [\partial_i {}^\alpha v_j(\mathbf{r}, \omega) \partial_i {}^\beta v_j^*(\mathbf{r}, \omega) + \partial_i {}^\alpha v_j(\mathbf{r}, \omega) \partial_j {}^\beta v_i^*(\mathbf{r}, \omega)] d^3r \quad (39)$$

$$= 2k_B \delta(\omega - \omega') \int_{\mathcal{V}} \phi_{\alpha\beta}(\mathbf{R}, \mathbf{r}, \omega) T(\mathbf{r}) d^3r. \quad (40)$$

In (39) we used the Fourier transform of (15a). Setting the magnitude of $\langle b_\alpha \rangle$ and $\langle b_\beta^* \rangle$ to one, we finally obtain the noise correlation tensor in the form

$$\langle \xi_\alpha(\mathbf{R}, \omega) \xi_\beta^*(\mathbf{R}, \omega') \rangle = k_B \mathcal{T}_{\alpha\beta}(\mathbf{R}, \omega) \mathcal{Z}_{\alpha\beta}(\mathbf{R}, \omega) \delta(\omega - \omega'), \quad (41)$$

where $\mathcal{T}_{\alpha\beta}$ is the frequency-dependent noise temperature defined by the spatial average of the temperature field $T(\mathbf{r})$ performed with the dissipation tensor $\phi_{\alpha\beta}$,

$$\mathcal{T}_{\alpha\beta}(\mathbf{R}, \omega) \equiv \frac{\int_{\mathcal{V}} \phi_{\alpha\beta}(\mathbf{R}, \mathbf{r}, \omega) T(\mathbf{r}) d^3r}{\int_{\mathcal{V}} \phi_{\alpha\beta}(\mathbf{R}, \mathbf{r}, \omega) d^3r}. \quad (42)$$

Summing up, we have arrived at the generalized Langevin equation for the particle (translational and angular) velocity \mathbf{b}

$$\mathbf{L} \cdot \dot{\mathbf{b}}(t) = - \int_{-\infty}^t \mathcal{Z}(\mathbf{R}, t - t') \cdot \mathbf{b}(t') dt' + \boldsymbol{\xi}(t) + \mathbf{f}_{\text{ext}}(t), \quad (43)$$

where the tensor \mathbf{L} combines the particle mass and moment of inertia, $\mathcal{Z}(t)$ is the time-dependent friction tensor, and $\boldsymbol{\xi}(t)$ is a Gaussian noise having vanishing mean and correlations given by Eqs. (15) and (42).

In order to determine Eq. (15), in principle one should consider Eq. (12c) with the appropriate boundary conditions.

Usually, these would consist in imposing constant temperatures at the outer boundaries and the continuity of the normal heat flux across the particle surface, i.e.,

$$\kappa_p \mathbf{n} \cdot \nabla T|_{\mathcal{S}_{\text{in}}} + q = \kappa \mathbf{n} \cdot \nabla T|_{\mathcal{S}_{\text{out}}}, \quad (44)$$

with q an optional heat flux released by the particle. If the heat sources are independent of the particle ($q = 0$), e.g., if they are placed at the outer boundaries of the fluid, the temperature field will generally depend on the instantaneous particle position. Nevertheless, in most practical cases the thermal conductivities of particle and solvent (κ_p and κ , respectively) will be such that the feedback of the particle motion onto the temperature field (which is of the maximum relative strength $O(\kappa_p/\kappa - 1)$ close to the particle surface [see [35], Eq. (24)]) can be treated as a small correction to the overall temperature field in the solvent. If the particle itself acts as the heat source, so that $q \neq 0$ in Eq. (44), like in hot Brownian motion [26,36], the temperature field can be calculated once and for all in the particle frame (advection terms arising from the change of frame can again be neglected). Therefore, Eqs. (41)–(43) can be taken to entirely describe the particle dynamics. The higher-order corrections should remain relatively small, if not negligible, for all practical purposes.

IV. ANALYTIC EXAMPLE: PARTICLE IN A LINEAR TEMPERATURE FIELD

We now consider a concrete example to illustrate the formal results of the previous section. Namely, we seek the Langevin equation for a spherical particle of radius a in an unbounded fluid with a constant temperature gradient of magnitude C , externally imposed along the z spatial direction,

$$T(\mathbf{r}) = T_0 + Cz. \quad (45)$$

For the sake of the argument, we consider a particle whose thermal conductivity is comparable to that of the solvent, i.e., $\kappa_p \simeq \kappa$ (e.g., a glass particle in water), so that its presence does not alter (45). If $\eta[T(\mathbf{r})] \simeq \eta$ is taken constant, which is a good approximation for water under moderate heating conditions, Eq. (12b) is independent of $T(\mathbf{r})$ and the problem can be fully worked out analytically. Due to the spherical symmetry enjoyed by the momentum equations (12b) and (5), no hydrodynamic coupling exists between different space directions and between angular and translational dynamics, i.e., $\phi_{\alpha\beta} = \text{diag}(\phi_{\alpha\beta})$. In the following we thus focus on the translational motion only. Moreover, the particle experiences a homogeneous fluid friction in view of (34) and $\phi_{\alpha\beta}$ being independent of \mathbf{R} .

In order to calculate $\mathcal{T}_{\alpha\beta} = \text{diag}(\mathcal{T}_{\alpha\beta})$, it is convenient to obtain the dissipation function $\phi_{z'z'}$ for a particle moving along a fixed \hat{z}' direction, where the prime denotes the particle frame (arbitrarily rotated with respect to the unprimed laboratory frame), and express the fluid temperature field in primed coordinates. Using the standard solution of the time-dependent Stokes equation (12b) for a sphere moving with unit velocity [17], one arrives at

$$\phi_{z'z'}(\mathbf{r}', \omega) = \eta[\cos^2 \theta' A(r', \omega) + \sin^2 \theta' B(r', \omega)], \quad (46)$$

where r' is the distance from the particle center, θ' is the polar angle measured from \hat{z}' , and A and B are known functions [36]

whose explicit form is not required here. Taking \hat{z}' parallel to \hat{z} , so that the fluid temperature reads in the particle frame

$$T(\mathbf{R} + \mathbf{r}') = T_0 + C(Z + r' \cos \theta'),$$

we find for the noise temperature in the z direction

$$\begin{aligned} \mathcal{T}_{zz}(Z, \omega) &= \frac{\int_{r' \geq a} \phi_{z'z'}(\mathbf{r}', \omega) T(\mathbf{R} + \mathbf{r}') d^3 r'}{\int_{r' \geq a} \phi_{z'z'}(\mathbf{r}', \omega) d^3 r'} \\ &= T_0 + CZ = T(Z), \end{aligned}$$

because the integral over the polar angle in the numerator vanishes. The physical reason lies in the symmetry of the flow field under reversal of the particle velocity, i.e., the transformation $\theta' \rightarrow \pi - \theta'$. By symmetry the noise temperatures in the directions perpendicular to \hat{z} are identical, i.e., $\mathcal{T}_{xx} = \mathcal{T}_{yy}$, and they are found by taking \hat{z}' parallel to \hat{x} . This choice renders the fluid temperature in the particle frame in the form

$$T(\mathbf{R} + \mathbf{r}') = T_0 + C(Z + r' \sin \theta' \cos \phi'),$$

which yields

$$\mathcal{T}_{xx}(Z, \omega) = T_0 + CZ = T(Z),$$

because the integral of $\phi_{z'z'}$ over the azimuthal angle vanishes. This is due to the spherical symmetry of the particle that produces a dissipation function that is (for constant η) axially symmetric with respect to \hat{z}' . Summing up, Eq. (43) for the translational motion reduces to

$$m \dot{\mathbf{V}}(t) = - \int_{-\infty}^t \mathcal{Z}(t-t') \mathbf{V}(t') dt' + \boldsymbol{\xi}(Z, t) + \mathbf{f}_{\text{ext}}, \quad (47)$$

where the noise temperature boils down to the local fluid temperature $\langle \xi_\alpha(t) \xi_\beta(0) \rangle = k_B T(Z) \mathcal{Z}(t) \delta_{\alpha\beta}$. The history-dependent friction is the Basset-Boussinesq force [17]. Namely, $\mathcal{Z}(t)$ contains an instantaneous contribution $6\pi\eta a \delta(t)$, corresponding to the Stokes friction, and a power-law term $\sim t^{-3/2}$, accounting for the finite relaxation time of fluid momentum.³

To clarify the role played by the position-dependent noise in Eq. (47), it is useful to examine the long-time diffusive behavior of the particle. It is obtained by retaining only the Stokes term⁴ in $\mathcal{Z}(t)$ and taking the overdamped limit of the resulting memoryless Langevin equation

$$m \dot{\mathbf{V}} = -\frac{1}{\mu} \mathbf{V} + \mathbf{f}_{\text{ext}} + \sqrt{2k_B T(Z)/\mu} \hat{\boldsymbol{\xi}}, \quad (48)$$

where $\mu \equiv (6\pi\eta a)^{-1}$ is the particle mobility and $\hat{\boldsymbol{\xi}}$ is a Gaussian white noise of unit variance. The overdamped limit, which is valid on time scales such that $dt \gg m\mu$, follows from adiabatic elimination in Eq. (48) of the fast variable \mathbf{V} [37,38],⁵

$$\dot{\mathbf{R}} = \mu \mathbf{f}_{\text{ext}} + \sqrt{2\mu k_B T(Z)} \hat{\boldsymbol{\xi}}. \quad (49)$$

³In fact, $\mathcal{Z}(t)$ includes also a derivative of a δ function that produces an effective added mass, stemming from fluid incompressibility [17].

⁴The memory effects in (47) can safely be dropped if $\rho_0/\rho_p \ll 1$, ρ_p being the particle density, which gives the relative magnitude of the power-law decay compared to the Stokes term [4,36].

⁵The multiplicative noise has to be interpreted in the Itô sense [41].

To see that the fluid temperature gradient appears on a par with the external forces we translate Eq. (49) to the equation for the density field $\rho(\mathbf{r}, t)$ of a dilute ensemble of Brownian particles (or, equivalently, to the Fokker-Planck equation for the single-particle probability density function) [39,40]

$$\begin{aligned} \partial_t \rho &= \nabla \cdot (\mu k_B T \nabla \rho + \mu \rho k_B \nabla T - \mu \mathbf{f}_{\text{ext}} \rho) \\ &\equiv \nabla \cdot (D \nabla \rho + D_T \nabla T - \mu \mathbf{f}_{\text{ext}} \rho). \end{aligned} \quad (50)$$

It differs from an isothermal advection-diffusion equation by virtue of the thermodiffusion flux $D_T \nabla T$. The thermodiffusion coefficient D_T is by definition positive and much smaller than what is usually measured in colloidal systems [35]. The discrepancy in the magnitude of the effect arises because under typical experimental conditions D_T depends strongly on the surface and solvation properties of the solute (e.g., dispersion, depletion, and electric-double-layer forces), which would have to be subsumed in the boundary conditions in a systematic microscopic derivation, but cannot be found within a hydrodynamic derivation. In fact, the value of D_T here obtained pertains to a dilute ideal solute in local equilibrium with the fluid, as one can see by inspecting the steady-state solution of (50) in the absence of external forces

$$\rho(\mathbf{r}) \propto \frac{1}{k_B T(\mathbf{r})}, \quad (51)$$

which indeed corresponds to the local version of the state equation of an ideal gas in mechanical equilibrium [39,40].

In conclusion, we have shown the validity of the standard Langevin description of Brownian motion in a linear temperature field when the viscosity is assumed to be constant. The fact that the noise temperature becomes a frequency-independent scalar and local in space, as usually postulated [27,28], originates from the high degree of symmetry of the system, but will not be true for generic $T(\mathbf{r})$. For example, a radial temperature field emanating from a heated particle suffices to produce a noise temperature with a rich frequency spectrum [36]. Clearly, the possibility to obtain exact analytic results hinges on the constancy of η . In general, corrections stemming from the neglected temperature dependence can be calculated as perturbations to the time-dependent Stokes equation or through semianalytic methods for the case of radial temperature fields [26].

V. DISCUSSION

We have analyzed the fluctuating hydrodynamic equations for a Brownian particle suspended in solvents with moderate temperature gradients. The main result obtained in Sec. II is that, on the scale relevant for the description of Brownian motion, it is sufficient to consider fluctuations of the solvent hydrodynamic fields around their local equilibrium state to linear order. In particular, the solvent velocity and temperature fields are found to evolve independently. This is traced back to two conditions. First, heat and momentum diffusion, rather than advection, is the dominant transport mode in the fluid, as testified by the small Reynolds and Péclet numbers, namely, $\text{Re} \simeq 10^{-3}$ and $\text{Pe} \simeq 10^{-2}$. Second, commonly realized temperature gradients induce negligible relative density variations of order $\epsilon_1 \simeq 10^{-2}$. The ensuing ineffectiveness of the momentum-temperature coupling has a

remarkable consequence on the Langevin noise ξ . Namely, its nonequilibrium energy spectrum is only a result of the spatial inhomogeneity of the random stress tensor τ , which is governed by the deterministic temperature field $T(\mathbf{r}, t)$. Qualitatively, this could have been anticipated by recalling that the most important enhancement of fluctuations in nonequilibrium fluids is due to (nonlinear) convective couplings⁶ that dominate on long wavelengths, beyond the Brownian scale [43]. Yet the characteristic energy spectrum $k_B T_{ij}$ governing the Brownian noise shares with them the distinctive features of nonequilibrium fluctuations [44], namely, their long-range nature and their dependence on the mechanical transport properties of the fluid, as encoded in the dissipation tensor $\phi_{\alpha\beta}$. Moreover, because $\phi_{\alpha\beta}$ is sensitive to the particle shape and size via the boundary condition (5), the noise temperature is ultimately a joint property of solvent *and* solute. This is in contrast to the results by Golestanian and Ajdari [45] for the long-time diffusion of a Brownian particle in temperature gradients. Assuming the (pointlike) particle to be simply advected by the random flow field without causing any disturbance, Golestanian and Ajdari identify the particle velocity fluctuations with those of the fluid and thus miss the essential near-field (finite-size) contributions that strongly depend on the particle parameters.

We conclude that an effective theory, which is linear in the particle-fluid momentum exchange and disregards stochastic fluctuations in the temperature field, is suitable to derive a contracted description for nonisothermal Brownian suspensions. The consequences of this result are more fully explored in Ref. [29], where the generalized Langevin equation (43) is derived by direct application of linear-response theory to the momentum of a Brownian particle and to (locally equilibrated) distant coarse-grained solvent volume elements.

Another important conclusion of our above calculations is that the Langevin noise ξ is characterized by Gaussian statistics. Non-Gaussian contributions to the fluctuations (around the vanishing mean of ξ) are peculiar features of out-of-equilibrium systems [46] that can appear only if nonlinear fluctuations are retained in the hydrodynamic equations or if the local-equilibrium assumption for the fluid is violated. Numerical simulations [47,48] have shown that the velocity fluctuations of a hot Brownian particle clearly exhibit Gaussian distributed velocity and (when placed in a harmonic potential) position fluctuations, even under extreme heating conditions and under narrow confinement. They thus corroborate our main result that a local-equilibrium linear fluctuating hydrodynamic theory with Gaussian noise provides a universal basis for deriving equations of motion for nonisothermal Brownian dynamics.

The vanishing average of the Langevin noise appearing in Eq. (43) implies that the important phenomenon of thermophoresis is absent in our discussion of nonisothermal Brownian dynamics. To be precise, the stationary distribution for the particle position associated with Eq. (43) will in general be nonuniform in space [as exemplified by Eq. (51) for a

⁶Such coupling between different hydrodynamic modes is the main culprit of nonequilibrium Casimir-like forces in confined fluids (see, e.g., [42]).

free particle in a constant temperature gradient] owing to the position-dependent noise strength. The corresponding weak kinematic thermodiffusion however should not be confused with what is commonly referred to as thermophoresis [49]. The notion refers to an effect that cannot be derived within any generic hydrodynamic approach, not even if density variations induced by temperature gradients are considered [17]. As explained in Sec. IV, it is a result of nonequilibrium molecular interaction forces at the particle-fluid interface and therefore remains absent for any hydrodynamic boundary condition that does not directly couple the velocity and temperature gradient at the particle surface [50]. Clearly, this does not preclude the introduction of thermophoresis into the hydrodynamic description by hand, e.g., by imposing a hydrodynamic slip velocity at the surface [51].

Finally, it is worth recalling the limitations incurred by the incompressibility assumption $\kappa_T \rightarrow 0$ made at the outset. While it is certainly adequate to describe the particle motion averaged over the whole frequency spectrum, it is bound to break down at high frequencies, comparable to the inverse time needed by a sound wave to propagate over a distance comparable to the particle radius. A corresponding effect that is well known in the equilibrium theory of Brownian motion is the failure of the incompressible theory to recover the mean-squared velocity $\langle V^2 \rangle = k_B T_0 / m$, as predicted by energy equipartition. Instead, it predicts $\langle V^2 \rangle = k_B T_0 / M$ with the renormalized mass $M > m$ accounting for the added inertia of the solvent backflow [4]. The discrepancy is straightforwardly resolved by observing that the limits $t \rightarrow 0$ and $\kappa_T \rightarrow 0$ do not commute in the evaluation of the equal-time velocity autocorrelation function [9,52]. Accordingly, we expect that the high-frequency predictions of our theory will deviate from measurements performed with compressible solvents,

but presumably only in a frequency range that is currently still difficult to access experimentally [12,13].

In summary, we showed that the weakness of advection effects implies that different hydrodynamic fields do not couple appreciably, on the Brownian scale. After deriving the appropriate theory of nonequilibrium fluctuating hydrodynamics, we identified a previously often overlooked nonlocality of the resulting generalized Langevin equation for the Brownian particle, originating from long-range correlations triggered by temperature inhomogeneities. While conceptually important, the effect was found to vanish for the practically important special case of a perfectly linear external temperature gradient. We further showed the Brownian noise to be Gaussian, which explains previous observations from numerical simulations. The thermodiffusion induced by the space dependence of the noise was pointed out to be subdominant with respect to the mesoscopic mechanisms of thermophoresis commonly governing experiments with colloidal suspensions. Altogether, we could thereby systematically vindicate an analytically tractable and practically useful theory for the Brownian motion of a colloidal particle in a nonisothermal solvent, which resembles very much that for the isothermal case. It only breaks down at very high frequencies, where sound modes become relevant, as much as the corresponding isothermal theory would.

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Effective temperatures of hot Brownian motionG. Falasco,^{1,*} M. V. Gnann,² D. Rings,³ and K. Kroy¹¹*Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, D-04009 Leipzig, Germany*²*Max Planck Institute for Mathematics in the Sciences, Inselstr. 22, 04103 Leipzig, Germany*³*Department of Physics and Astronomy, University of Leeds, LS2 9JT Leeds, United Kingdom*

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We derive generalized Langevin equations for the translational and rotational motion of a heated Brownian particle from the fluctuating hydrodynamics of its nonisothermal solvent. The temperature gradient around the particle couples to the hydrodynamic modes excited by the particle itself so that the resulting noise spectrum is governed by a frequency-dependent temperature. We show how the effective temperatures at which the particle coordinates and (angular) velocities appear to be thermalized emerge from this central quantity.

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I. INTRODUCTION

Hot Brownian motion [1] is the diffusive dynamics of a colloidal particle persistently maintained at higher temperature than the surrounding fluid, so that the fluid temperature field $T(\mathbf{r}) = T(r)$ decays radially around the particle. It is of practical relevance, e.g., for laser-heated suspended nanoparticles involved in several experimental applications ranging from particle trapping and tracking [2,3] to self-thermophoretic microswimmers [4,5]. Besides, it is also of considerable theoretical interest, since it can be thought of as an archetypical example of a system in contact with a nonisothermal bath, hence far from thermal equilibrium. Nevertheless, for important conceptual and practical purposes, the hot particle can often be treated like an equivalent Brownian particle in equilibrium, with appropriate effective transport coefficients.

In particular, it has been shown analytically [6,7] that free and confined diffusion of a hot spherical particle are, in the long-time limit, governed by effective “positional” temperatures, denoted by T^x and T^Θ for translation in the X direction and rotation along an angle Θ , respectively. The positional temperatures enter the effective Stokes-Einstein relations and Boltzmann factors for translation and rotation of the particle, respectively. Additionally, extensive numerical simulations [6,8] have shown that the Maxwellian (angular) velocity distribution and the short-time response of the hot Brownian particle are characterized by yet other, somewhat higher, effective temperatures, so-called kinetic temperatures T^v and T^Ω . None of these effective temperatures are generally equal to the solvent temperature $T_s \equiv T(r \rightarrow R)$ at the particle surface or to the ambient temperature $T_0 \equiv T(r \rightarrow \infty)$. This complex behavior has led to the conclusion that an effective Langevin description of hot Brownian motion is restricted to the Markov limit [8].

Here we show constructively how this limitation can be overcome, starting from the fluctuating hydrodynamics of a solvent maintained at local thermal equilibrium with a temperature field $T(\mathbf{r})$. On this basis, we derive the generalized Langevin equation (GLE) for a heated spherical particle. Conceptually, nonspherical particles can be treated along the

same lines, albeit with additional complications [7]. The most conspicuous feature of the theory is a frequency-dependent noise temperature $\mathcal{T}(\omega)$ [9]. It arises from the hydrodynamic coupling between the particle and distant solvent volume elements that are locally equilibrated at different temperatures $T(\mathbf{r})$. From this central quantity analytical predictions for the mentioned kinetic and positional effective temperatures are derived.

The characteristic frequency scales that primarily select the dominant modes from the “temperature spectrum” $\mathcal{T}(\omega)$ are (for a translating sphere of mass m , density ρ_p , and radius R)

$$\omega_f \equiv \frac{2\nu}{R^2} \quad \text{and} \quad \omega_p \equiv \frac{6\pi\eta R}{m} = \frac{9\varrho}{4\rho_p}\omega_f, \quad (1)$$

namely, the inverse time scale for vorticity diffusion across the particle, and the inverse Stokes relaxation time of the particle momentum, respectively. The former characterizes how efficiently the particle momentum is spatially dispersed in a solvent of kinematic viscosity $\nu = \eta/\varrho$ and density ϱ , and the latter how, as a result, the motion of the particle adjusts to that of the fluid. The meaning of slow and fast processes, or low and high frequencies of the noise spectrum, is primarily provided by these rates. It should be clear, though, that any externally imposed additional time scale that interferes with these rates can be expected to yield additional features.

The paper is structured as follows. In the next section we introduce the theoretical model of a Brownian particle in a nonisothermal solvent. We then sketch the contraction of the coupled solvent-particle system to the GLE for the particle motion, alone. Details of the calculation are given in Appendix A. In Sec. III we examine the frequency-dependent temperatures $\mathcal{T}(\omega)$ that govern the Langevin noise for the translational and rotational degrees of freedom of a heated sphere and give a qualitative physical interpretation of their functional form, while some technicalities are deferred to Appendix B. From this central quantity, we derive the effective rotational and translational kinetic temperatures of a free particle in Sec. IV. We analyze their explicit dependence on the characteristic time scales for the velocity relaxation of the particle and the solvent by varying their density ratio. Also we regain the known positional temperatures for translation and rotation [6,7] as the low-frequency limits of $\mathcal{T}(\omega)$. In Sec. V, we consider a hot Brownian particle trapped in a harmonic

*gianmaria.falasco@itp.uni-leipzig.de

potential. While the known effective-equilibrium description can be retrieved in the Markov limit, we point out that the kinetic and positional temperatures may differ from those in the free case for very stiff traps, due to the interference of the characteristic trap time scale with the rates defined in Eq. (1). We conclude with a summary and short outlook.

II. FLUCTUATING HYDRODYNAMICS OF A HEATED PARTICLE

We consider a spherical particle of radius R immersed in an incompressible fluid of density ϱ . The time evolution of fluid momentum is described by the linearized fluctuating hydrodynamic equations [10–13]

$$\varrho \partial_t \mathbf{v}(\mathbf{r}, t) - \nabla \cdot \boldsymbol{\sigma}(\mathbf{r}, t) = \nabla \cdot \boldsymbol{\tau}(\mathbf{r}, t), \quad (2a)$$

$$\nabla \cdot \mathbf{v}(\mathbf{r}, t) = 0, \quad (2b)$$

$$\mathbf{v}(\mathcal{S}, t) = \mathbf{V}(t) + \boldsymbol{\Omega}(t) \times \mathbf{r} \text{ on } \mathcal{S}, \quad (2c)$$

where the velocity field \mathbf{v} of the fluid is defined in the volume \mathcal{V} outside the particle and the no-slip boundary condition on the particle surface \mathcal{S} is imposed by Eq. (2c). The stress tensor $\boldsymbol{\sigma}$ has components

$$\sigma_{ij}(\mathbf{r}, t) = -p(\mathbf{r}, t)\delta_{ij} + 2\eta(\mathbf{r}, t)\Gamma_{ij}(\mathbf{r}, t), \quad (3)$$

where p is the pressure and $\Gamma_{ij} = (\partial_i v_j + \partial_j v_i)/2$ the shear rate tensor, with the dynamic viscosity η . The incompressibility condition Eq. (2b) can be eliminated by expressing p (and thus $\boldsymbol{\sigma}$) as a functional of the flow field \mathbf{v} . Finally, the thermal noise is represented by a zero-mean Gaussian random stress tensor $\boldsymbol{\tau}$ that vanishes on the particle surface [12] and otherwise obeys the fluctuation-dissipation relation

$$\langle \tau_{ij}(\mathbf{r}, t) \tau_{kl}(\mathbf{r}', t') \rangle = 2\eta(\mathbf{r}, t)k_B T(\mathbf{r}, t)\delta(\mathbf{r} - \mathbf{r}') \times \delta(t - t')(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \quad (4)$$

corresponding to a local equilibrium with the prescribed deterministic temperature field $T(\mathbf{r}, t)$ [14]. In general, the dynamical viscosity $\eta(\mathbf{r}, t)$ inherits some spatiotemporal dependence of $T(\mathbf{r}, t)$. The vectors $\mathbf{V}(t)$ and $\boldsymbol{\Omega}(t)$, denoting the translational and rotational velocity of the Brownian particle, couple to the solvent dynamics via the boundary condition (2c) on the particle surface \mathcal{S} . They evolve themselves according to Newton's equations of motion

$$m\dot{\mathbf{V}}(t) = \mathbf{F}(t) + \mathbf{F}_e(t), \quad (5a)$$

$$I\dot{\boldsymbol{\Omega}}(t) = \mathbf{T}(t) + \mathbf{T}_e(t), \quad (5b)$$

where m is the mass of the particle, I the moment of inertia, \mathbf{F}_e and \mathbf{T}_e are the external force and torque, and \mathbf{F} and \mathbf{T} are the hydrodynamic force and torque exerted by the fluid, defined by

$$\mathbf{F}(t) = - \int_{\mathcal{S}} \boldsymbol{\sigma}(\mathbf{r}, t) \cdot \mathbf{n} d^2r, \quad (6a)$$

$$\mathbf{T}(t) = - \int_{\mathcal{S}} \mathbf{r} \times (\boldsymbol{\sigma}(\mathbf{r}, t) \cdot \mathbf{n}) d^2r, \quad (6b)$$

with \mathbf{n} the inner radial unit vector. Note that we have suppressed the time dependence of \mathcal{S} in Eqs. (2c) and (6) in order to make the above set of equations linear not only in the

flow field but also in the particle velocity. See Refs. [15,16] for a discussion of the validity of linear hydrodynamics in relation to Brownian motion. We also suppress the corresponding time-dependent thermal advection, by requiring the deterministic part of the temperature field to obey the stationary heat equation in the comoving frame,

$$\nabla^2 T(\mathbf{r}) = 0, \quad T(\mathbf{r}) = T_0 + \Delta T \text{ on } \mathcal{S}, \quad T(r \rightarrow \infty) = T_0. \quad (7)$$

This technical simplification and other implicit idealizations, such as neglecting the viscous heating due to the particle motion with respect to the housekeeping heat and taking the heat conductivity of the solvent to be constant, can be justified for common experimental conditions, such as those realized for laser-heated nanoparticles in water [1,17]. Together with the prescription Eq. (7), the system (2)–(4) then entirely describes the time evolution of the fluid and the heated Brownian particle. Notice that the fluctuations in the fluid temperature are irrelevant in our hydrodynamic description as they do not couple with momentum fluctuations thanks to the incompressibility assumption. Consequently, only the deterministic fluid temperature $T(\mathbf{r})$ is considered. The solution of Eq. (7) is the radial field:

$$T(\mathbf{r}) = T_0 + \Delta T R/r. \quad (8)$$

While the following derivation does not strictly depend on the specific form of $T(\mathbf{r})$ (as long as it does not depend on the particle velocity), and even an explicit externally imposed dependence on time could be included, we restrict the discussion in the following sections to this paradigmatic case.

We now proceed to contract the description of fluid plus particle into an equation for the particle alone. We rewrite the hydrodynamic forces introduced in Eq. (5) in the form

$$\mathbf{F} \equiv \mathbf{F}_d + \boldsymbol{\xi}^T, \quad (9a)$$

$$\mathbf{T} \equiv \mathbf{T}_d + \boldsymbol{\xi}^R \quad (9b)$$

to account for contributions $\boldsymbol{\xi}$ independent of the particle velocity that are expected to arise due to the inhomogeneity of Eq. (2a). By Eq. (2), $\mathbf{v}(\mathbf{r}, t)$ is a linear functional of $\mathbf{V}(t')$ and $\boldsymbol{\Omega}(t')$ with $-\infty < t' < t$, so in view of Eq. (6) this implies that the systematic components \mathbf{F}_d and \mathbf{T}_d are linear functionals of $\mathbf{V}(t')$ and $\boldsymbol{\Omega}(t')$, respectively, with $-\infty < t' < t$. Hence, we can write

$$\mathbf{F}_d(t) = - \int_{-\infty}^t \zeta(t-t') \mathbf{V}(t') dt', \quad (10)$$

$$\mathbf{T}_d(t) = - \int_{-\infty}^t \gamma(t-t') \boldsymbol{\Omega}(t') dt', \quad (11)$$

where $\zeta(t)$ and $\gamma(t)$ are positive, time-symmetric memory kernels accounting for the time-dependent drag on the particle [12]. Equations (5) then take the GLE form

$$m\dot{\mathbf{V}}(t) = - \int_{-\infty}^t \zeta(t-t') \mathbf{V}(t') dt' + \boldsymbol{\xi}^T(t) + \mathbf{F}_e(t), \quad (12)$$

$$I\dot{\boldsymbol{\Omega}}(t) = - \int_{-\infty}^t \gamma(t-t') \boldsymbol{\Omega}(t') dt' + \boldsymbol{\xi}^R(t) + \mathbf{T}_e(t), \quad (13)$$

once we identify $\xi^{T,R}$ as the Langevin noise, whose statistical properties have to be derived from those of the random stress tensor τ .

For better readability, the actual calculation is detailed in Appendix A, and only the main results and their physical interpretations are given in the main text. We focus mostly on the translational motion, but the rotational case is very analogous. It is moreover convenient to switch to the frequency representation defining, for a generic function $g(\omega)$, the Fourier transform $g(\omega) \equiv \int_{-\infty}^{\infty} e^{i\omega t} g(t) dt$ and the half-Fourier transform $g^+(\omega) \equiv \int_0^{\infty} e^{i\omega t} g(t) dt$.

To complete the contraction, we compare the energy dissipated by the fluid friction acting on the particle at a mean velocity $\langle \mathbf{V}(\omega) \rangle$

$$\zeta(\omega) \delta_{ij} \langle V_i(\omega) \rangle \langle V_j^*(\omega) \rangle = 2 \int_{\mathcal{V}} \phi^T(\mathbf{r}, \omega) d^3 r, \quad (14)$$

with the correlation function of the energy supplied by the random force at frequencies ω and ω' :

$$\begin{aligned} & \langle \xi_i^T(\omega) \xi_j^{T*}(\omega') \rangle \langle V_i(\omega) \rangle \langle V_j^*(\omega') \rangle \\ & = 2k_B \delta(\omega - \omega') \int_{\mathcal{V}} \phi^T(\mathbf{r}, \omega) T(\mathbf{r}) d^3 r. \end{aligned} \quad (15)$$

From Appendix A, we have quoted the representation in terms of the dissipation function,

$$\phi^T(\mathbf{r}, \omega) \equiv \eta (\partial_i u_j \partial_i u_j^* + \partial_i u_j \partial_j u_i^*), \quad (16)$$

which gives the energy dissipated by the fluid at position \mathbf{r} and frequency ω in terms of the average flow field $\mathbf{u}(\mathbf{r}, \omega)$. Setting the arbitrary average velocity of the particle to unity, Eq. (14) allows one to calculate the memory kernel $\zeta(\omega)$ in terms of the spatial integral of the dissipation function $\phi^T(\mathbf{r}, \omega)$.

From Eqs. (14) and (15) we then find the relation

$$\begin{aligned} & \langle \xi_i^T(\omega) \xi_j^{T*}(\omega') \rangle \langle V_i(\omega) \rangle \langle V_j^*(\omega') \rangle \\ & = k_B \mathcal{T}^T(\omega) \zeta(\omega) \delta_{ij} \delta(\omega - \omega') \langle V_i(\omega) \rangle \langle V_j^*(\omega') \rangle \end{aligned} \quad (17)$$

with

$$\mathcal{T}^T(\omega) \equiv \frac{\int_{\mathcal{V}} \phi^T(\mathbf{r}, \omega) T(\mathbf{r}) d^3 r}{\int_{\mathcal{V}} \phi^T(\mathbf{r}, \omega) d^3 r}. \quad (18)$$

Since $\phi^T(\mathbf{r}, \omega)$ is a quadratic function of $\langle \mathbf{V}(\omega) \rangle$ (see Appendix B) the ratio in Eq. (18) is independent of $\langle \mathbf{V}(\omega) \rangle$. Moreover, as the particle velocity $\langle \mathbf{V}(\omega) \rangle$ is arbitrary it can be deleted in Eq. (17), which renders Eq. (17) in the form of a generalized fluctuation-dissipation relation:

$$\langle \xi_i^T(\omega) \xi_j^{T*}(\omega') \rangle = k_B \mathcal{T}^T(\omega) \zeta(\omega) \delta_{ij} \delta(\omega - \omega'). \quad (19)$$

According to Eq. (A9), the Langevin noise ξ^T is Gaussian distributed with mean zero. Therefore Eq. (19) fully characterizes the noise statistics. Analogous results hold for the rotational motion. They are obtained by substituting $\zeta \rightarrow \gamma$ in Eq. (19) and $\phi^T \rightarrow \phi^R$ in the definition (18).

III. THE NOISE TEMPERATURE $\mathcal{T}(\omega)$

Equation (18) defines the frequency-dependent noise temperature that is the central quantity for the Brownian motion under nonisothermal conditions. Its nonlocal nature manifests

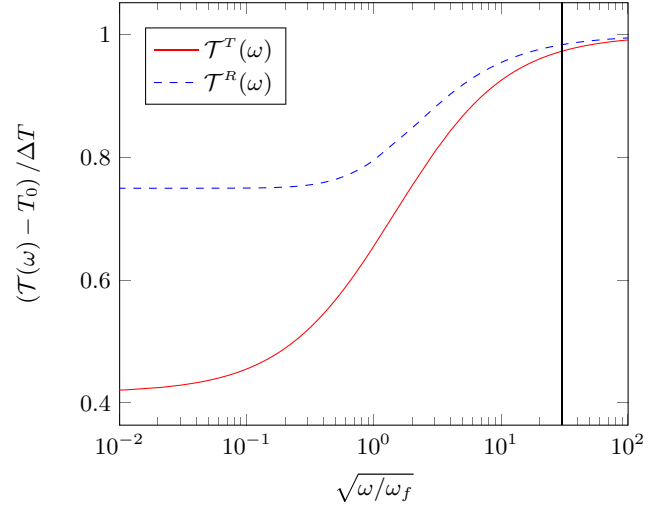


FIG. 1. (Color online) The universal frequency-dependent noise temperatures for the motion of a Brownian particle, obtained by the definitions (16) and (18) assuming a temperature-independent solvent viscosity η . The rotational noise temperature (blue/top line) is given by the exact expression Eq. (B3), while the translational one (red/bottom line) is obtained by numerical integration of Eqs. (18) and (B1). The vertical solid line indicates the characteristic frequency beyond which the finite compressibility of water would matter for a solid particle of radius $R \simeq 100$ nm.

itself in the weighted average over the temperature field $T(\mathbf{r})$, with the dissipation function determining how strongly the diverse local temperatures in the surroundings affect the Brownian motion of the particle at the origin.

Clearly, the noise autocorrelation can always be cast in such a form by defining a suitable function $\mathcal{T}(\omega)$ that measures the violation of the equilibrium fluctuation-dissipation relation. Here the nontrivial statement is that $\mathcal{T}(\omega)$ is explicitly derived from an underlying hydrodynamic description. Moreover, in the next sections, we will show that $\mathcal{T}(\omega)$ plays the role of a frequency-dependent effective temperature, in the sense that dynamical isothermal relations can directly be extended to the nonisothermal case if the temperature T_0 is replaced by $\mathcal{T}(\omega)$.

Contenting ourselves with explicit evaluations to leading order in the temperature heterogeneity $T(\mathbf{r}) - T_0$, we can in the following neglect a possible temperature dependence of the viscosity, which would affect our results to subleading order, only. Figure 1 shows the frequency-dependent temperatures $\mathcal{T}(\omega)$ for the translational and the rotational motion of a sphere, which are derived in Appendix B assuming constant heat conductivity and viscosity, i.e., Eq. (7) and $\eta(\mathbf{r}) = \eta$. As a consequence, η cancels in Eq. (18), and the obtained noise temperatures are universal functions independent of the solvent properties. All the subsequent results are derived under the latter approximation.

To gain a physical understanding of the functional form of $\mathcal{T}(\omega)$, consider its origin from the hydrodynamic coupling between the particle and distant solvent volume elements that are locally equilibrated at different temperatures $T(\mathbf{r})$. In our low-Reynolds number approximation, the exchange of momentum is dominated by vorticity diffusion [18] with the

diffusivity given by the kinematic viscosity $\nu \equiv \eta/\rho$. This defines the inverse characteristic time scale $\omega_f \equiv 2\nu/R^2$ for fluid transport over distances on the order of the particle radius, as introduced in Eq. (1).

Low-frequency fluctuations are those with $\omega \ll \omega_f$, during which the vorticity spreads out considerably from the particle. Since the translational field is more long-range than the rotational one ($\mathbf{u}^T \sim 1/r$ versus $\mathbf{u}^R \sim 1/r^2$), the translational noise is effectively cooler, as it involves an average over farther, i.e., cooler, regions of fluid. Ultimately, in the limit $\omega \rightarrow 0$, we find that the noise temperatures reduce to the effective temperatures $T_{\text{HBM}}^{x,\theta}$ known to characterize the overdamped hot Brownian motion of the positions and angles, respectively [6,7], for which we employ the shorthand notation

$$\begin{aligned} T^x &\equiv \mathcal{T}^T(0) = T_0 + \frac{5}{12}\Delta T, \\ T^\theta &\equiv \mathcal{T}^R(0) = T_0 + \frac{3}{4}\Delta T. \end{aligned}$$

In contrast, during *high-frequency fluctuations* with $\omega \gg \omega_f$, fluid momentum cannot diffuse significantly from the particle surface. The vorticity emanating from a particle oscillating at frequency ω cannot penetrate the fluid beyond the skin depth $k_0^{-1} \equiv (2\nu/\omega)^{1/2} \ll R$, resulting in an exponential decay $\phi(r,\omega) \propto e^{-k_0(r-R)}$ of the dissipation function; see Eqs. (B1) and (B2). Therefore, the average in Eq. (18) is essentially restricted to a thin skin of solvent around the particle surface, and the noise temperatures tend towards the surface temperature $T_s = T_0 + \Delta T$ for large ω . However, note that the finite compressibility becomes relevant at very high frequencies. As a consequence, the noise temperature may deviate significantly from our predictions for frequencies larger than the inverse of the time it takes a sound wave in the solvent to traverse a distance R [15,19].

It is worth mentioning another peculiarity implied by the incompressibility assumption. To accelerate a particle in an incompressible fluid, the displaced fluid has to be moved from the front to the back of the particle. Therefore, the layer of fluid that is set into motion never collapses completely onto the particle surface, as it does for rotation at high frequencies. While the noise temperature is not affected, since the bulk dissipation turns out to be subdominant (see Appendix B), incompressibility results in a renormalized particle mass [10,12]:

$$M = m + m\varrho/(2\varrho_p). \quad (20)$$

The added mass in Eq. (20), owing to the inertia of the displaced fluid, becomes relevant in the following. In the next sections we analyze some immediate implications of the above results for the dynamics of a hot Brownian sphere that is either freely diffusing or trapped in a confining potential.

IV. THE KINETIC TEMPERATURE

The GLEs (5a) and (5b) both contain a Gaussian noise satisfying a fluctuation-dissipation relation with constant effective temperatures in the high-frequency limit. Therefore, one may expect to find Maxwell-Boltzmann distributions of

translational and angular velocities under stationary conditions, which is corroborated by molecular dynamics simulations [6,7]. We thus define the kinetic temperatures such that the stationary averages of the velocities satisfy

$$\frac{3}{2}k_B T^v \equiv \frac{1}{2}M\langle \mathbf{V}^2 \rangle, \quad \frac{3}{2}k_B T^\Omega \equiv \frac{1}{2}I\langle \boldsymbol{\Omega}^2 \rangle, \quad (21)$$

which reduce to the equipartition theorem with $T^\Omega = T^v = T_0$ in case of a constant fluid temperature $T(\mathbf{r}) \equiv T_0$. For simplicity, we concentrate on the translational motion, in the following, but the same procedure applies also to the rotational motion.

From the Fourier transform of Eq. (12) in the absence of an external force,

$$-i\omega m \mathbf{V}(\omega) = -\zeta^+(\omega)\mathbf{V}(\omega) + \boldsymbol{\xi}^T(\omega), \quad (22)$$

we derive the velocity spectral density

$$C_v(\omega) \equiv \langle \mathbf{V}(\omega) \cdot \mathbf{V}(-\omega) \rangle = |R_v(\omega)|^2 C_\xi^T(\omega). \quad (23)$$

Here

$$C_\xi^T(\omega) = 3k_B \mathcal{T}^T(\omega) \zeta(\omega) \quad (24)$$

is the noise spectral density and $R_v(\omega)$ is the velocity response defined as

$$R_v(\omega) = \frac{1}{\zeta^+(\omega) - i\omega M}. \quad (25)$$

The Wiener-Khinchine theorem then gives the velocity auto-correlation function

$$\langle \mathbf{V}(t) \cdot \mathbf{V}(0) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} |R_v(\omega)|^2 C_\xi^T(\omega) e^{-i\omega t} d\omega, \quad (26)$$

from which the translational kinetic temperature T^v , defined in Eq. (21), follows as

$$T^v = \frac{M}{\pi} \int_0^{\infty} |R_v(\omega)|^2 \mathcal{T}^T(\omega) \zeta(\omega) d\omega, \quad (27)$$

since the integrand is an even function of ω .

To further evaluate this result, we introduce into the response R_v the explicit expression for the memory kernel of a sphere translating in an incompressible fluid with no-slip boundary conditions [12]:

$$\zeta^+(\omega) = 6\pi\eta R \left[1 + (1-i)\sqrt{\frac{R^2\omega}{2\nu}} - iR^2\omega/9\nu \right]. \quad (28)$$

The first term in the brackets is the usual Stokes friction $\zeta^+(\omega=0) \equiv \zeta$, the second describes the vorticity diffusion and gives rise to the long-time tails [20,21]. The third term accounts for the mentioned mass renormalization [Eq. (20)]. With the

notation $x^2 = \omega/\omega_f$, Eq. (27) now reads

$$T^v = \frac{1}{\pi} \int_0^\infty \frac{4\alpha x(x+1)\mathcal{T}^T(x)}{(1+x)^2 + x^2(1+\alpha x)^2} dx, \quad (29)$$

which depends on the particle-to-fluid density ratio via the parameter $\alpha \equiv 2(2\varrho_p/\varrho + 1)/9$. The same procedure gives the rotational kinetic temperature

$$T^\Omega = \frac{1}{\pi} \int_0^\infty \frac{12\beta x(1+2x+2x^2)(3+6x+6x^2+2x^3)\mathcal{T}^R(x)}{\{(3+6x+6x^2+2x^3)^2 + x^4[2(1+x)+3\beta(1+2x+2x^2)]^2\}} dx \quad (30)$$

with $\beta \equiv 2\varrho_p/(15\varrho)$.

Equations (29) and (30) can be integrated numerically using the translational and rotational noise temperatures $\mathcal{T}(\omega)$ introduced in Sec. III. The results are shown in Fig. 2. The kinetic temperatures are seen to depend on the density ratio ϱ_p/ϱ . To understand this, consider a translating sphere. In the Markov limit, its velocity relaxes within the Stokes time, corresponding to the relaxation rate

$$\omega_p \equiv \frac{\zeta}{M} = \frac{6\pi\eta R}{M} = \frac{9\varrho}{4\varrho_p}\omega_f, \quad (31)$$

introduced in Eq. (1). The density ratio thus relates the characteristic time for the kinematic equilibration of the particle with the fluid, i.e., the time it takes to spread the particle momentum to a fluid mass comparable to the particle mass, to the time it takes to spread its momentum to a fluid volume comparable to the particle volume. Accordingly, the kinematic equilibration affects either a small or large fluid volume compared to the particle size, suggesting a kinetic temperature close to the temperature T_s at the particle surface or close to the stationary effective temperature T^x , respectively.

Indeed, if $\varrho_p/\varrho \ll 1$, only the upper part of the spectrum $\mathcal{T}(\omega)$ contributes to the kinetic temperatures, as seen from Eqs. (29) and (30), where the integrand contributes significantly only for $x \gg 1$. Hence, the rotational kinetic temperature

T^Ω approaches the surface temperature:

$$T^\Omega \sim \mathcal{T}^R(\infty) = T_0 + \Delta T = T_s \quad \text{for } \varrho_p/\varrho \rightarrow 0. \quad (32)$$

Due to the mass renormalization [Eq. (20)] the translational kinetic temperature T^v always remains somewhat below this limit, though. Although the noise temperature attempts to shake the particle with a strength proportional to the surface temperature T_s , the particle cannot move without exciting a long-range flow field that ultimately increases its own inertia. This effect limits the velocity fluctuations of the particle to a nonuniversal apparent “equipartition” temperature T^v that depends on the density ratio ϱ_p/ϱ and attains the limit

$$T^v \simeq T_0 + 0.86 \Delta T < T_s \quad \text{for } \varrho_p/\varrho \rightarrow 0. \quad (33)$$

As a consequence, the translational particle velocity never thermalizes to the fluid temperature at the particle surface.

In the opposite limit, $\varrho_p/\varrho \gg 1$, the frequency-dependent terms in Eq. (28), which are proportional to $R^2\omega_p/\nu = 2\omega_p/\omega_f \ll 1$, become small. In this limit, the kinetic temperature approaches the stationary values of the respective effective noise temperatures $\mathcal{T}(0)$, which coincide with the known temperatures for the configurational degrees of freedom, represented by the positional and orientational coordinates X and Θ [6,7] (see Sec. III). They determine the translational and rotational diffusion coefficient of the hot Brownian particle, e.g., for translation,

$$\begin{aligned} D &= \lim_{t \rightarrow \infty} \frac{1}{6} \frac{d}{dt} \langle [X(t) - X(0)]^2 \rangle \\ &= \frac{1}{2} \int_{-\infty}^{\infty} \langle \mathbf{V}(t) \cdot \mathbf{V}(0) \rangle dt = \frac{1}{2} C_V(\omega = 0). \end{aligned} \quad (34)$$

Using Eqs. (23)–(25) and (28), we recover (to leading order in the temperature increment ΔT , i.e., not accounting for the temperature-induced spatial variations in the viscosity) the generalized Einstein relation [6]

$$D_{\text{HBM}} = \frac{k_B \mathcal{T}^T(\omega)}{\zeta^+(\omega)} \Big|_{\omega=0} = \frac{k_B(T_0 + \frac{5}{12} \Delta T)}{6\pi\eta R}. \quad (35)$$

The same reasoning applies to the orientation Θ . Hence, we see that for a hot Brownian particle that is much denser than the solvent, the kinetic temperatures reduce to the effective configurational temperatures,

$$T^{v,\Omega} \sim \mathcal{T}^{T,R}(0) = T^{x,\Theta} \quad \text{for } \varrho_p/\varrho \rightarrow \infty. \quad (36)$$

Moreover, in any case, both the translational and rotational velocities of a hot spherical particle can be statistically

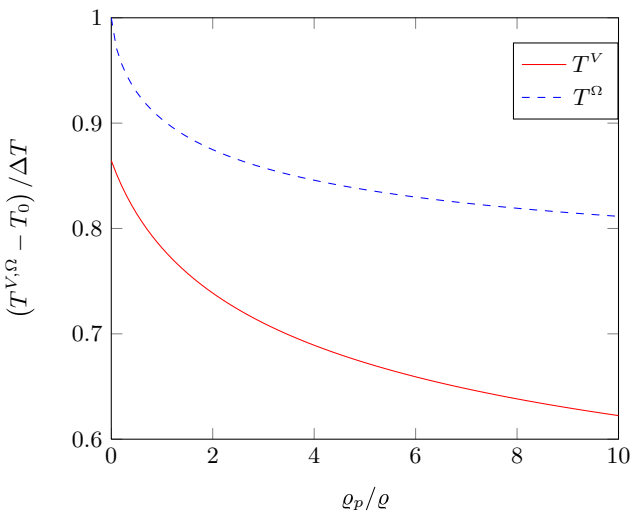


FIG. 2. (Color online) Rotational (blue/top line) and translational (red/bottom line) kinetic temperature as function of the density ratio ϱ_p/ϱ .

characterized by a (nonuniversal) Maxwell-Boltzmann distribution

$$P(\mathbf{V}, \boldsymbol{\Omega}) \propto \exp\left(-\frac{M\mathbf{V}^2}{2k_B T^v} - \frac{I\boldsymbol{\Omega}^2}{2k_B T^\omega}\right) \quad (37)$$

with effective temperatures that depend on the density ratio ϱ_p/ϱ , in agreement with the fact that probability distributions of nonequilibrium ensembles explicitly depend on the dynamics of the system.

V. PARTICLE IN A HARMONIC POTENTIAL

The discussion of the previous section can be repeated for a particle trapped in a harmonic potential. While the kinetic temperature of a free particle is determined by the competition between the vorticity diffusion time ω_f^{-1} and the Stokes relaxation time ω_p^{-1} introduced in Eq. (1), a sufficiently narrow confining potential introduces an additional interfering time scale. In the following, we examine more closely the case of translational diffusion in confinement, but qualitatively similar results can be derived for the rotational case. The parabolic confinement potential $\mathcal{U}(\mathbf{X}) = K\mathbf{X}^2/2$ gives rise to the trap relaxation time

$$\omega_t^{-1} = 6\pi\eta R/K = \omega_p/\omega_0^2, \quad (38)$$

where $\omega_0^2 = K/m$ is the undamped oscillation frequency. With $\mathbf{F}_e = -K\mathbf{X}$, the Fourier-transformed Eq. (12),

$$-m\omega^2 \mathbf{X}(\omega) = i\omega\zeta^+(\omega)\mathbf{X}(\omega) - K\mathbf{X}(\omega) + \boldsymbol{\xi}(\omega),$$

yields the spectral density

$$C_x(\omega) \equiv \langle \mathbf{X}(\omega) \cdot \mathbf{X}(-\omega) \rangle = |R_x(\omega)|^2 C_\xi(\omega), \quad (39)$$

where the positional response function is defined by

$$R_x(\omega) = \frac{1}{m(\omega_0^2 - \omega^2) - i\omega\zeta^+(\omega)}. \quad (40)$$

We use the relation

$$\langle \mathbf{V}(t) \cdot \mathbf{V}(0) \rangle = -\frac{d^2}{dt^2} \langle \mathbf{X}(t) \cdot \mathbf{X}(0) \rangle$$

between the stationary correlation functions for position and velocity in frequency space, $C_V(\omega) = \omega^2 C_X(\omega)$. The kinetic temperature, as defined in Eq. (21), follows as

$$\begin{aligned} T^v &= \frac{M}{\pi} \int_0^\infty \omega^2 |R_x(\omega)|^2 \mathcal{T}^T(\omega) \zeta(\omega) d\omega \\ &= \frac{1}{\pi} \int_0^\infty \frac{4\alpha x^5 (x+1) \mathcal{T}^T(x)}{x^4(1+x)^2 + (x^3 + \alpha x^4 - \omega_t/\omega_f)^2} dx. \end{aligned} \quad (41)$$

The result is again integrated numerically and depicted in Fig. 3. Clearly, if $\omega_t \ll \omega_f$, which means that the potential is not effective while the velocity is relaxing, we recover the result for free diffusion [Eq. (29)]. This should be the case for an optically trapped nanoparticle in water under standard experimental conditions. Indeed, for a gold particle with $R \simeq 100$ nm, assuming a trap stiffness $K = 10^{-6}$ Nm $^{-1}$ [22], we estimate $\omega_t/\omega_f \simeq 10^{-2}$. The velocity relaxation time decreases as we increase the ratio ω_t/ω_f , resulting in a higher kinetic temperature. When $\omega_t \gg \omega_f$ the narrow confinement eventually overrides the inertia of the particle motion due

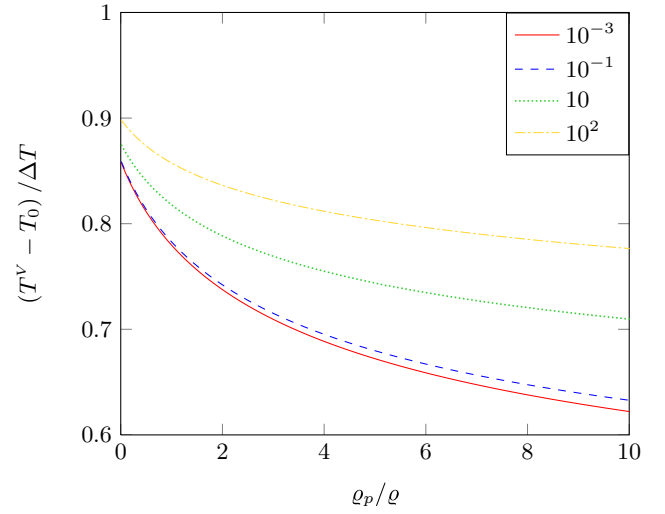


FIG. 3. (Color online) Kinetic temperature T^v of a particle in harmonic confinement, as given by Eq. (41) for various $\omega_t/\omega_f = 10^{-3}, \dots, 10^2$. For $\omega_t/\omega_f \lesssim 10^{-1}$, T^v is hardly distinguishable from the kinetic temperature of a free particle.

to its effective mass M , so that the kinetic temperature T^v approaches the surface temperature T_s . Similarly as for the particle velocity, we define the positional temperature of a hot Brownian particle in a harmonic potential via the generalized equipartition theorem,

$$\frac{3}{2}k_B T^x \equiv \frac{1}{2}\omega_0^2 m \langle \mathbf{X}^2 \rangle, \quad (42)$$

where the average is taken with respect to the stationary distribution. Using Eqs. (39) and (40) we straightforwardly obtain

$$\begin{aligned} T^x &= \frac{\omega_0^2 m}{\pi} \int_0^\infty |R_x(\omega)|^2 \mathcal{T}^T(\omega) \zeta(\omega) d\omega \\ &= \frac{1}{\pi} \int_0^\infty \frac{4(\omega_t/\omega_f)x(x+1)\mathcal{T}^T(x)}{x^4(1+x)^2 + (x^3 + \alpha x^4 - \omega_t/\omega_f)^2} dx. \end{aligned} \quad (43)$$

This result is integrated numerically and plotted in Fig. 4. Again, if $\omega_t \ll \omega_f$, we recover the configurational temperature of a free particle, since the integrand in Eq. (43) is sharply peaked at $x \ll 1$, corresponding to $\omega \ll \omega_f$. Physically, the relaxation in the potential takes place quasistatically with respect to the free hot Brownian motion, which can then be represented in the Markov approximation, in perfect analogy to the equilibrium case. The corresponding Langevin equation is

$$\zeta \dot{\mathbf{X}} = -\nabla \mathcal{U} + \boldsymbol{\xi}, \quad \langle \xi_i(t) \xi_j(t') \rangle = 2D_{\text{HBM}} \delta(t-t') \delta_{ij},$$

and its stationary solution is the generalized Boltzmann distribution

$$P(\mathbf{X}) \propto \exp\left(-\frac{\mathcal{U}(\mathbf{X})}{k_B T^x}\right).$$

with the effective temperature

$$T^x = \zeta D_{\text{HBM}} = T_0 + \frac{5}{12} \Delta T \quad (44)$$

of free hot Brownian motion [6] (originally denoted by T_{HBM}).

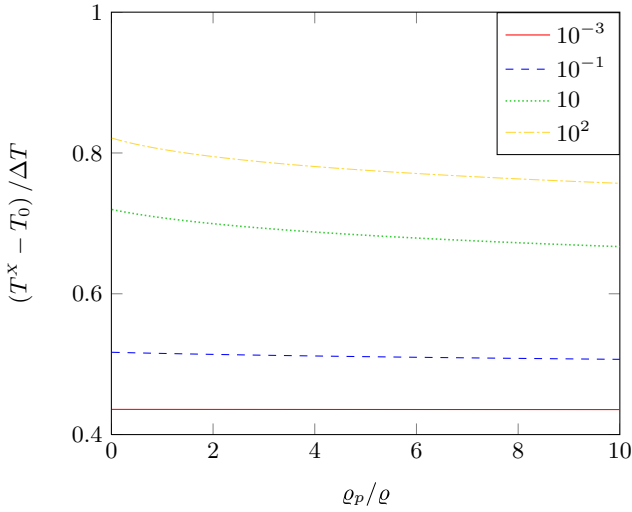


FIG. 4. (Color online) Positional temperature T^x of a particle in harmonic confinement, as given by Eq. (43) for various $\omega_t/\omega_f = 10^{-3}, \dots, 10^2$. At small ω_t/ω_f the temperature is independent of ρ_p/ρ .

In contrast, if $\omega_t \approx \omega_p$ the potential interferes with the relaxation of the particle, resulting in a higher T^x than in the free case. Eventually, in the extreme limit $\omega_t \gg \omega_p$, the integral peaks near ω_t , and T^x approaches the kinetic temperature T^v (nonuniformly in ρ_p/ρ). It is moreover worth noting that the stationary probability distribution can in any case still be written in the form of Eq. (37), albeit with nonuniversal temperatures T^v and T^x that generally depend on the density ratio ρ_p/ρ and on the stiffness K of the potential. Analogous conclusions hold for the rotational degrees of freedom.

VI. CONCLUSION

Starting from the fluctuating hydrodynamic description of the solvent, which we required to be in local thermal equilibrium with an inhomogeneous temperature field $T(\mathbf{r})$, we have derived a generalized Langevin equation for the motion of a Brownian suspended particle. While the discussion was limited to the important case of hot Brownian motion, where $T(\mathbf{r})$ decays radially around the particle, essentially the same reasoning applies to more general temperature profiles [9]. As a consequence of the nonisothermal conditions, the noise temperature $\mathcal{T}(\omega)$ characterizing the strength of the stochastic Langevin forces becomes frequency dependent and differs between different degrees of freedom, which couple to different hydrodynamic modes. We remark that the frequency-dependent noise temperature is not merely defined, as it is customary, through the violation of equilibrium ensemble properties of the particle position and velocity, e.g., the broken proportionality between response and equilibrium correlation functions expressed by the (first-kind) fluctuation-dissipation theorem [23,24]. Rather, $\mathcal{T}(\omega)$ is derived upon contraction of the underlying stochastic description and its physical origin is fully understood in terms of nonequilibrium hydrodynamic fluctuations of the viscous solvent.

From the noise temperature we derived approximate expressions for the effective temperatures at which the rotational and translational degrees of freedom of a spherical particle appear to thermalize. Explicit numerical results have been limited to first order in the temperature increment ΔT , so that the temperature dependence of the fluid viscosity could be neglected. We found the (angular) velocities to be Maxwell-Boltzmann distributed with nonuniversal, but explicitly known, effective temperatures. The violation of the equilibrium (second-kind) fluctuation-dissipation theorem given by Eq. (19), i.e., the broken proportionality between noise correlation and memory kernel, is ultimately the reason why effective temperatures appear in the equilibrium-like distributions of the particle position and velocity [9]. In the long-time limit we regained previous results for the configurational temperatures governing free and weakly confined hot Brownian motion.

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APPENDIX A: DERIVATION OF THE GLE'S NOISE AUTOCORRELATION FUNCTION

Extending the calculation presented in Ref. [13] to a nonisothermal solvent, we derive expressions (14) and (15) in Sec. II for the translational motion. The same procedure can be applied separately to rotational motion bearing in mind that, due to linearity and spherical symmetry, the flow field \mathbf{v} can be divided into the two independent fields \mathbf{v}^T and \mathbf{v}^R generated, respectively, by the particle translation and rotation, and satisfying the boundary conditions:

$$\begin{aligned} \mathbf{v}^T(\mathbf{r}, t) &= \mathbf{V}(t) \quad \text{on } \mathcal{S}, \\ \mathbf{v}^R(\mathbf{r}, t) &= \boldsymbol{\Omega}(t) \times \mathbf{r} \quad \text{on } \mathcal{S}. \end{aligned}$$

Since we focus on the translational motion only, we omit the superscript T. Using Eq. (10), the Fourier transform of the generalized Langevin equation (12) reads

$$-i\omega m \mathbf{V}(\omega) = -\zeta^+(\omega) \mathbf{V}(\omega) + \boldsymbol{\xi}(\omega) + \mathbf{F}_e(\omega)$$

and may be rewritten as

$$-i\omega m \mathbf{V}(\omega) = \mathbf{f}(\omega) + \tilde{\mathbf{f}}(\omega) + \mathbf{F}_e(\omega), \quad (\text{A1})$$

where we have divided the force exerted by the fluid into deterministic $\mathbf{f}(\omega)$ and random $\tilde{\mathbf{f}}(\omega)$ components:

$$\mathbf{f}(\omega) \equiv -\zeta^+(\omega) \langle \mathbf{V}(\omega) \rangle, \quad (\text{A2a})$$

$$\tilde{\mathbf{f}}(\omega) \equiv -\zeta^+(\omega) \tilde{\mathbf{V}}(\omega) + \boldsymbol{\xi}(\omega), \quad (\text{A2b})$$

with $\mathbf{V} \equiv \langle \mathbf{V} \rangle + \tilde{\mathbf{V}}$. It is easy to see that $\mathbf{f}(\omega)$ is the force exerted by the deterministic flow field $\mathbf{u} \equiv \langle \mathbf{v} \rangle$, the solution

of

$$i\omega\varrho\mathbf{u}(\mathbf{r},\omega) + \nabla \cdot \boldsymbol{\sigma}(\mathbf{r},\omega) = 0, \quad (\text{A3a})$$

$$\nabla \cdot \mathbf{u}(\mathbf{r},\omega) = 0, \quad (\text{A3b})$$

$$\mathbf{u}(\mathbf{r},\omega) = \langle \mathbf{V}(\omega) \rangle \quad \text{on } \mathcal{S}, \quad (\text{A3c})$$

while $\tilde{\mathbf{f}}(\omega)$ is the force exerted by the stochastic flow field $\tilde{\mathbf{u}} \equiv \mathbf{v} - \langle \mathbf{v} \rangle$, the solution of

$$i\omega\varrho\tilde{\mathbf{u}}(\mathbf{r},\omega) + \nabla \cdot \tilde{\boldsymbol{\sigma}}(\mathbf{r},\omega) = -\nabla \cdot \boldsymbol{\tau}(\mathbf{r},\omega), \quad (\text{A4a})$$

$$\nabla \cdot \tilde{\mathbf{u}}(\mathbf{r},\omega) = 0, \quad (\text{A4b})$$

$$\tilde{\mathbf{u}}(\mathbf{r},\omega) = \tilde{\mathbf{V}}(\omega) \quad \text{on } \mathcal{S}. \quad (\text{A4c})$$

This splitting of equations and boundary conditions is again allowed by the linearity of the problem. In the following calculation, in order to ease the notation, we omit the arguments \mathbf{r} and ω of the hydrodynamic fields where there is no possibility of confusion.

We start by calculating twice the energy dissipated by the particle moving at velocity $\langle \mathbf{V}(\omega) \rangle$:

$$\begin{aligned} \langle V_i(\omega) \rangle [\zeta^+(\omega) + \zeta^{+*}(\omega)] \langle V_i^*(\omega) \rangle &\stackrel{(\text{A2a})}{=} -[f_i(\omega) \langle V_i^*(\omega) \rangle + f_i^*(\omega) \langle V_i(\omega) \rangle] \\ &\stackrel{(6)}{=} \langle V_i^*(\omega) \rangle \int_{\mathcal{S}} \sigma_{ij} n_j d^2r + \langle V_i(\omega) \rangle \int_{\mathcal{S}} \sigma_{ij}^* n_j d^2r \\ &\stackrel{(\text{A3c})}{=} \int_{\mathcal{S}} u_i^* \sigma_{ij} n_j d^2r + \int_{\mathcal{S}} u_i \sigma_{ij}^* n_j d^2r \\ &= \int_{\mathcal{V}} \partial_j (u_i^* \sigma_{ij}) d^3r + \int_{\mathcal{V}} \partial_j (u_i \sigma_{ij}^*) d^3r \\ &\stackrel{(\text{A3a})}{=} \int_{\mathcal{V}} (\sigma_{ij} \partial_j u_i^* + \sigma_{ij}^* \partial_j u_i) d^3r \\ &\stackrel{(\text{A3b})}{=} \int_{\mathcal{V}} 2\eta (\Gamma_{ij} \partial_j u_i^* + \Gamma_{ij}^* \partial_j u_i) d^3r \\ &= 2 \int_{\mathcal{V}} \phi(\mathbf{r},\omega) d^3r, \end{aligned} \quad (\text{A5})$$

where in Eq. (A5) we employed the divergence theorem and in Eq. (A6) we defined the dissipation function:

$$\phi(\mathbf{r},\omega) \equiv \eta(\mathbf{r}) (\partial_i u_j \partial_j u_i^* + \partial_i u_j^* \partial_j u_i)(\mathbf{r},\omega).$$

Since $\zeta(\omega) = 2\Re\zeta^+(\omega) = \zeta^+(\omega) + \zeta^{+*}(\omega)$, being $\zeta(t)$ real and time symmetric, we can rewrite Eq. (A6) in the following form:

$$\zeta(\omega) \delta_{ij} \langle V_i(\omega) \rangle \langle V_j^*(\omega) \rangle = 2 \int_{\mathcal{V}} \phi(\mathbf{r},\omega) d^3r. \quad (\text{A7})$$

This proves Eq. (14). We proceed with the evaluation of the energy supplied by the random force $\boldsymbol{\xi}(\omega)$:

$$\begin{aligned} \xi_i(\omega) \langle V_i(\omega) \rangle &\stackrel{(\text{A2b})}{=} [\tilde{f}_i(\omega) + \zeta^+(\omega) \tilde{V}_i(\omega)] \langle V_i(\omega) \rangle \\ &\stackrel{(\text{A2a})}{=} \tilde{f}_i(\omega) \langle V_i(\omega) \rangle - f_i(\omega) \tilde{V}_i(\omega) \\ &\stackrel{(6)}{=} -\langle V_i(\omega) \rangle \int_{\mathcal{S}} \tilde{\sigma}_{ij} n_j d^2r + \tilde{V}_i(\omega) \int_{\mathcal{S}} \sigma_{ij} n_j d^2r \\ &\stackrel{(\text{A3c})(\text{A4c})}{=} -\int_{\mathcal{S}} u_i \tilde{\sigma}_{ij} n_j d^2r + \int_{\mathcal{S}} \tilde{u}_i \sigma_{ij} n_j d^2r \\ &= -\int_{\mathcal{V}} \partial_j (u_i \tilde{\sigma}_{ij}) d^3r + \int_{\mathcal{V}} \partial_j (\tilde{u}_i \sigma_{ij}) d^3r \\ &\stackrel{(\text{A3a})(\text{A4a})}{=} -\int_{\mathcal{V}} \tilde{\sigma}_{ij} \partial_j u_i d^3r + \int_{\mathcal{V}} \sigma_{ij} \partial_j \tilde{u}_i d^3r + \int_{\mathcal{V}} u_i \partial_j \tau_{ij} d^3r \\ &\stackrel{(\text{A3b})(\text{A4b})}{=} \int_{\mathcal{V}} u_i \partial_j \tau_{ij} d^3r = -\int_{\mathcal{V}} \tau_{ij} \partial_j u_i d^3r \end{aligned} \quad (\text{A8})$$

In Eq. (A8) we made use again of the divergence theorem. Summing up,

$$\xi_i(\omega) \langle V_i(\omega) \rangle = -\int_{\mathcal{V}} \tau_{ij}(\mathbf{r},\omega) \partial_j u_i(\mathbf{r},\omega) d^3r, \quad (\text{A9})$$

which asserts that $\xi(\omega)$ is Gaussian with vanishing mean, being the integral of the deterministic quantity $\partial_j u_i$ times the zero-mean Gaussian field τ_{ij} . Using Eq. (A9) we evaluate the noise correlation function:

$$\begin{aligned} \langle \xi_i(\omega) \xi_j^*(\omega') \rangle \langle V_i(\omega) \rangle \langle V_j^*(\omega') \rangle &= \int_{\mathcal{V}} d^3 r' \int_{\mathcal{V}} d^3 r \partial_j u_i(\mathbf{r}, \omega) \langle \tau_{ij}(\mathbf{r}, \omega) \tau_{kl}^*(\mathbf{r}', \omega') \rangle \partial_l u_k^*(\mathbf{r}', \omega') \\ &= 2k_B \delta(\omega - \omega') \int_{\mathcal{V}} \eta (\partial_i u_j \partial_l u_j^* + \partial_i u_j \partial_j u_i^*) T d^3 r \\ &= 2k_B \delta(\omega - \omega') \int_{\mathcal{V}} \phi(\mathbf{r}, \omega) T(\mathbf{r}) d^3 r. \end{aligned} \quad (\text{A10})$$

In Eq. (A10) we used the Fourier transform of Eq. (4) together with $\tau_{kl}^*(\mathbf{r}', \omega') = \tau_{kl}(\mathbf{r}', -\omega')$, since τ is real. This proves Eq. (15).

APPENDIX B: HYDRODYNAMICS OF A TRANSLATION AND ROTATING SPHERE

1. Translational motion

The Fourier transform of the flow field generated by a sphere translating with velocity $\langle V(\omega) \rangle \mathbf{e}_z$ reads in polar coordinates (r, φ, θ) [11, p. 623]:

$$\mathbf{u}^T(r, \theta, \omega) = \frac{1}{r} \left[\sin \theta \left(g + r \frac{dg}{dr} \right) \mathbf{e}_\theta - 2g \cos \theta \mathbf{e}_r \right],$$

with

$$g(r, \omega) = \frac{3\langle V(\omega) \rangle R}{2(kr)^2} \left\{ (ikr - 1) e^{ik(r-R)} - \left[1 + ikR - \frac{1}{3}(kR)^2 \right] \right\},$$

where $k = (1 + i)k_0$, and $k_0 = \sqrt{\omega/2\nu}$ is the inverse of the characteristic fluid diffusion length. The associated dissipation function is

$$\phi^T = \eta \left(\frac{12}{r^4} \cos^2 \theta \left| g - r \frac{dg}{dr} \right|^2 + \sin^2 \theta \left| \frac{d^2 g}{dr^2} \right|^2 \right),$$

that becomes after integration over θ :

$$\begin{aligned} &\int_0^\pi \phi^T(r, \theta, \omega) \sin \theta d\theta \\ &= \frac{3\eta |\langle V(\omega) \rangle|^2 R^2}{2k_0^4 r^8} \left\{ 5[9 + 2k_0 R(9 + k_0 R(9 + 2k_0 R(3 + k_0 R)))] \right. \\ &\quad + e^{-2k_0(r-R)} [45 + 2k_0 r [45 + k_0 r (45 + k_0 r (30 + k_0 r (15 + 2k_0 r (3 + k_0 r)))] \\ &\quad - 2e^{-k_0(r-R)} [(45 + 45k_0 R + 15k_0(3 + 2k_0 R(3 + k_0 R))r + 12k_0^3 R(3 + 2k_0 R)r^2 + 2k_0^3(-3 + 2k_0^2 R^2)r^3) \cos[k_0(R - r)] \\ &\quad \left. - k_0(-15R(3 + 2k_0 R) + 15(3 - 2k_0^2 R^2)r + 36k_0(1 + k_0 R)r^2 + 2k_0^2(3 + 2k_0 R(3 + k_0 R))r^3) \sin[k_0(R - r)] \right] \}. \end{aligned} \quad (\text{B1})$$

Notice that Eq. (B1) displays a term which does not decay with an exponential cutoff but only algebraically as $1/r^8$. But its contribution to $\mathcal{T}(\omega)$ actually diminishes at high frequencies, $k_0 \rightarrow \infty$. In order to obtain $\mathcal{T}(\omega)$ we numerically integrate Eq. (18) together with Eq. (B1). The result is shown in Fig. 1.

2. Rotational motion

The Fourier transform of the flow field generated by a sphere rotating with angular velocity $\langle \Omega(\omega) \rangle \mathbf{e}_z$ reads [10, p. 91]

$$\mathbf{u}^R(r, \theta, \omega) = \frac{\langle \Omega(\omega) \rangle R^3}{r^2} \sin \vartheta \frac{1 - ikr}{1 - ikR} e^{i[k(r-R)]} \mathbf{e}_\varphi \equiv f(r, \vartheta, \omega) \mathbf{e}_\varphi.$$

The associated dissipation function $\phi^R(\mathbf{r}, \omega)$ is

$$\begin{aligned} \phi^R &= \frac{\eta}{r^2} (|r \partial_r f - f|^2 + |\partial_\vartheta f - \cot \vartheta f|^2) \\ &= \frac{\eta |\langle \Omega(\omega) \rangle|^2 R^6 [9 + 18k_0 r + 18(k_0 r)^2 + 12(k_0 r)^3 + 4(k_0 r)^4] \sin^2 \vartheta e^{-2k_0(r-R)}}{r^6 [1 + 2k_0 R + 2(k_0 R)^2]}. \end{aligned} \quad (\text{B2})$$

Notice in Eq. (B2) the exponential cutoff where the fluid's diffusion characteristic length k_0^{-1} appears. Using Eqs. (18) and (B2) we obtain the first-order approximation in ΔT for the noise temperature of rotational motion:

$$\frac{\mathcal{T}^R(\omega) - T_0}{\Delta T} = \frac{9 + 18k_0R + 18(k_0R)^2 + 12(k_0R)^3 - 8(k_0R)^4 E_1(2k_0R)e^{2k_0R}}{4[3 + 6k_0R + 6(k_0R)^2 + 2(k_0R)^3]}, \quad (\text{B3})$$

where $E_1(x) = \int_1^\infty dy e^{-xy}/y$ is the exponential integral. The result is plotted in Fig. 1.

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Chapter 3

Nonequilibrium virial relations and generalized equation of state

In the previous chapter we have seen that the usual energy equipartition between conjugate variables (we are accustomed to in equilibrium) is broken when the equilibrium FDT is violated *and* memory effects are present. In this chapter we turn to the wide class of systems that enjoys an infinite timescale separation with respect to their thermal baths. We show that the steady states of these Markovian systems, which are equilibrium's closer relatives, satisfy a set of practically meaningful general relations, so-called mesoscopic virial equations, involving conjugated pairs of microscopic or mesoscopic (e.g. collective) variables. Summation of a mesoscopic virial equation over all degrees of freedom generates the virial theorem. It serves as a passkey to nonequilibrium equations of state linking conventional thermodynamic variables to steady dissipative currents.

The relevance of such relations is twofold. On the one hand, it is of fundamental interest to look for equilibrium-like concepts which carry over to a reasonably large class of stationary nonequilibria, and thus may help in constructing a generalized thermodynamic theory that copes with dissipative effects [92–94]. On the other, various technological applications call for the understanding of energy repartition and pressure under inhomogeneous conditions in devices operating far from equilibrium. Examples are microcantilever-based sensors [95] and gravitational wave detectors [96], which work subjected to thermal gradients, and mechanical micro-engines fueled by active environments (e.g. bacterial bath) [97], respectively.

To obtain the mesoscopic virial equations we exploit the kinematic nature (independent of statistics) of the derivation of the virial theorem, which generalizes to propagators of nonequilibrium steady states. This property is in general largely overlooked, arguably because the virial theorem is commonly viewed as a mere consequence of the equipartition law,

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = \left\langle q_i \frac{\partial \mathcal{H}}{\partial q_i} \right\rangle = k_B T, \quad (3.1)$$

that holds for any pair of conjugated variables q_i and p_i of a system with Hamiltonian \mathcal{H} in canonical equilibrium at temperature T . In textbooks [67, 98] the virial theorem is then derived by summing (3.1) over the N degrees of freedom of the system and introducing the total i -th force $-\partial \mathcal{H} / \partial q_i = F_i$. For Hamiltonians quadratic in the momenta, it establishes the equality between twice the average kinetic energy and the

so-called virial¹,

$$\left\langle \sum_{i=1}^N \frac{p_i^2}{m_i} \right\rangle = - \left\langle \sum_{i=1}^N F_i q_i \right\rangle, \quad (3.2)$$

whose value coincides with $Nk_B T$.

However, one should not be misled into thinking that the virial theorem pertains to equilibrium situations only. On the contrary, the fact that a purely mechanical equivalent of (3.2) can be proved for stable bounded systems [99], should suggest that (3.2) may hold in generic stationary states. In the mechanical virial theorem statistical averages are replaced by time averages over the stationary system's trajectory, irrespective of the nature of the forces (conservative or not) that maintain such state. It is even tempting to accept this result as a statistical statement without further ado, only appealing to the ergodic hypothesis, that is the equality of time and ensemble averages [100].

Stimulated by this heuristic logics, in [51] we obtain a nonequilibrium virial theorem by extending (3.1) to mesoscopic virial equations valid under generic stationary conditions. The derivation is based on the obvious fact that the time derivative of any averaged state observable $\mathcal{O}(\mathbf{q}(t), \mathbf{p}(t)) \equiv \mathcal{O}(t)$ vanishes in the stationary state. The derivative is conveniently calculated introducing the (backward) propagator, $\exp Lt$, which evolves mean observables² from an (arbitrary) initial time 0 to the observation time t :

$$0 = \frac{d}{dt} \langle \mathcal{O}(t) \rangle = \frac{d}{dt} \int d\mathbf{q}_0 d\mathbf{p}_0 \rho(\mathbf{q}_0, \mathbf{p}_0) e^{Lt} \mathcal{O}(\mathbf{q}_0, \mathbf{p}_0) = \langle L\mathcal{O}(t) \rangle. \quad (3.3)$$

A smart choice of the observable \mathcal{O} is then needed to generalized (3.1) to any (driven) Markovian dynamics, whose details appear implicitly in the generator L . For example, L coincides with the Liouville operator for Hamiltonian systems, and with the adjoint of the Fokker-Planck operator for Langevin systems. For the latter, when non-conservative forces f_i and multiple reservoirs at different temperatures T_i are present, choosing $\mathcal{O} = p_i q_i$ and $\mathcal{O} = p_i^2$ gives the mesoscopic virial equations,

$$\left\langle \frac{p_i^2}{m_i} \right\rangle = \left\langle q_i \left(\frac{\partial \mathcal{H}}{\partial q_i} - f_i \right) \right\rangle = k_B T_i + \frac{\dot{Q}_i}{\gamma_i}. \quad (3.4)$$

First, an extended equipartition law still exists between conjugated variables, which includes the Hamiltonian as well as non-conservative forces. Importantly, the effective friction and noise that model the interaction with the thermal baths drop out in the derivation, so that only the physical forces appear in the mesoscopic virial equation³. Second, the kinetic energy is not just proportional to the local temperature, but it is also increased by the heat flux \dot{Q}_i dissipated by f_i into the reservoir in the damping time $1/\gamma_i$. As a consequence, equipartition is in general restricted to the pair of conjugated coordinates of a single degree of freedom.

It is remarkable that, if the system is driven away from equilibrium only by baths at different temperatures ($f_i = 0$), then (3.4) keeps the form of a proper energy repartition. In [50, 51] we exploit this relation to study the energy distribution in the normal

¹For a homogeneous pairwise potential energy, $U_i(r) \sim r^a$, like gravity, the virial coincides with $a \langle \sum_{i=1}^N U_i \rangle$. For this reason, it is often employed in astrophysics.

²This corresponds to the Heisenberg picture of quantum mechanics, where the wave function (here the probability density) is fixed and the observable changes in time.

³This is a plus of the Langevin equations, which is not true for other thermostats, such as the Nose-Hoover one.

modes of (un)harmonic lattices under nonisothermal conditions. These prototypical systems are largely employed to study (anomalous) heat conduction under deterministic dynamics [31], but are rarely considered within a stochastic framework [101], e.g. to effectively model conduction in macroscopic solids. In our work we address the influence of the temperature profile T_i , the boundary conditions and the presence of small nonlinearities on the energy repartition between modes. For purely harmonic interactions we can also reverse the logics and device temperature gradients suitable for cooling or heating at will some specific set of modes.

Armed with (3.4) and the corresponding virial equation obtained by summing over i , in [51] we follow the conventional chain of arguments to derive generalized mechanical equations of states [67, 102]. For d dimensional systems with $n = N/d$ particles kept at fixed volume \mathcal{V} , it amounts to separating in the virial the internal forces $F_{\text{int},i}$ (interparticle interactions) from the external ones (e.g. confinement, gravity) and to identify the latter with the mean pressure \bar{P}_S on the container's surface⁴:

$$\bar{P}_S \mathcal{V} d = nk_B T + \left\langle \sum_i F_{\text{int},i} q_i \right\rangle + \frac{\dot{Q}}{\gamma}. \quad (3.5)$$

Here, the total heat flowing from the system into the bath, \dot{Q}/γ , supplements the usual equilibrium terms, i.e., the ideal gas and interaction contribution.

It is remarkable that a generalized state equation features thermodynamic variables together with dissipative fluxes. A similar upgrade of fluxes to state variables can be found in phenomenological theories aiming at describing far from equilibrium phenomena, such as rational and irreversible generalized thermodynamics [103, 104]. There, balance equations for the fluxes (derived by an extended entropy production function) are considered, which complement the usual equations for the mass, momentum and energy density. Even though justified by kinetic theory results⁵, these theories do not rest on such a sound and simple foundation as the one presented here. Also note that, our approach is far more conservative, since it is limited to stationary states, in which fluxes are independent of the system's history.

An instructive application of the equation of state (3.5) is presented in [51] for a fluid of self-propelled particles. These units, ranging from motile bacteria to artificial colloids, are capable of converting (stored or locally supplied) energy into directed motion [30]. Because the energy input happens isotropically at the particle scale, they differ fundamentally from other kinds of driven matter, such as sheared fluids, in which space symmetry is externally broken and the energy flux proceeds from large to small scales. When hydrodynamic interactions through the solvent are negligible, self-propulsion can be effectively model as a one-body non-conservative force [105] and the resulting Markovian dynamics fulfils the mesoscopic virial equation. The associated pressure equation turns out to depend (away from the thermodynamic limit) on the details of the confinement force [106, 107] through the heat flux \dot{Q} —showing how static properties of a nonequilibrium system are generally not independent of its dynamical aspects.

⁴To ease comparison with equilibrium we restrict ourselves to a single homogeneous bath with temperature T and damping rate γ . The only source of nonequilibrium is thus the driving f_i .

⁵Namely, Grad's 13 moment expansion of the Boltzmann equation [103].



PAPER

Mesoscopic virial equation for nonequilibrium statistical mechanics

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and DOI.G Falasco^{1,5,6}, F Baldovin^{2,3,4}, K Kroy⁵ and M Baiesi^{2,3}¹ Max Planck Institute for Mathematics in the Sciences, Inselstr. 22, D-04103 Leipzig, Germany² Dipartimento di Fisica ed Astronomia, Università di Padova, Via Marzolo 8, I-35131 Padova, Italy³ INFN, Sezione di Padova, Via Marzolo 8, I-35131 Padova, Italy⁴ CNISM—Sezione di Padova, Via Marzolo 8, I-35131 Padova, Italy⁵ Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, D-04009 Leipzig, Germany⁶ Author to whom any correspondence should be addressed.E-mail: falasco@itp.uni-leipzig.de, baldovin@pd.infn.it, klaus.kroy@itp.uni-leipzig.de and baiesi@pd.infn.it**Keywords:** nonequilibrium statistical mechanics, equations of state, virial theorem, Langevin dynamics**Abstract**

We derive a class of mesoscopic virial equations governing energy partition between conjugate position and momentum variables of individual degrees of freedom. They are shown to apply to a wide range of nonequilibrium steady states with stochastic (Langevin) and deterministic (Nosé–Hoover) dynamics, and to extend to collective modes for models of heat-conducting lattices. A macroscopic virial theorem ensues upon summation over all degrees of freedom. It allows for the derivation of generalised (nonequilibrium) equations of state that involve average dissipative heat flows besides genuine state variables, as exemplified for inertial Brownian motion with solid friction and overdamped active Brownian particles subject to inhomogeneous pressure.

1. Introduction

From equilibrium statistical mechanics we are accustomed to the idea that there is energy equipartition among all quadratic degrees of freedom of classical systems, and that the ‘energy bit’ corresponds to $k_B T/2$, half of the temperature times the Boltzmann constant. While momenta usually appear with the quadratic contribution of the kinetic energy in the Hamiltonian \mathcal{H} , for a position variable q_i one has more generally that it is the average of $q_i \partial_{q_i} \mathcal{H}$ which equals the energy bit. The sum over all degrees of freedom yields the virial theorem [1, 2], which connects the average total kinetic energy with the term $\sum_i \langle q_i \partial_{q_i} \mathcal{H} \rangle$ named virial by Clausius.

Out of equilibrium, the equipartition of energy is not granted. Indeed, recent experiments with heat-conducting metals show intriguing deviations from equipartition, related to enhancements of low-frequency vibrational modes that may become even ‘hotter’ than the highest boundary temperature [3]. Similar deviations from equipartition are observed for strongly heated cantilevers [4] and Brownian particles [5, 6]. These are some out of many manifestations of nontrivial effects characterizing systems driven far from thermodynamic equilibrium. They imply the need for a critical revisiting of results from equilibrium statistical mechanics, with the aim of finding generalisations to nonequilibrium conditions.

In this work we discuss a generalization of the equipartition theorem, formulated in the context of modern nonequilibrium physics. It takes the form of *mesoscopic virial equations* (MVEs), involving kinetic and dynamical aspects specific to pairs of momentum–position conjugate variables. A MVE determines how thermal energy is distributed between any such pair of variables. For Langevin dynamics, we discuss both the inertial and the overdamped versions of the equation; the former is easily extended to cover Nosé–Hoover dynamics for thermostated simulations. Summation of a MVE over all degrees of freedom generates the virial theorem, which we discuss also for the case of explicitly nonconservative forces. That the virial theorem holds at the microscopic level beyond thermal equilibrium should not come as a surprise, since it is a result derivable in classical mechanics without appealing to statistical arguments⁷. Here we show that one still finds significant virial

⁷ In classical mechanics the theorem involves time averages, which are customarily exchanged with ensemble averages under the ergodic assumption [7].

theorems, involving quantities with a clear physical meaning, even if microscopic degrees of freedom are coarse grained as in the mesoscopic models addressed below.

The simple mathematical derivations we employ are slightly different from the conventional line of arguments dating back to Chandrasekhar's work [2, 8]. The main novelty of our approach is that we work consistently in the context of nonequilibrium systems, and that our derivations easily carry over to deterministic thermostats. Moreover, we characterise energy partition even for collective macroscopic variables, such as single normal modes, out of equilibrium. We further show that our results allow for the derivation of generalised equations of state for nonequilibrium steady states. As an illustrative example, we provide a full derivation of the pressure equation for a well-known model of active matter [9].

2. Langevin dynamics

Consider N interacting particles evolving in d dimensions, with generalised coordinates $\{q_i, p_i\}$, with $i = 1, \dots, Nd$. Each degree of freedom has mass m_i and the total energy is given by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{Nd} \frac{p_i^2}{2m_i} + U(\{q_i\}), \quad (1)$$

where $U(\{q_i\})$ contains a confining potential energy that allows the system to reach a stationary state in the absence of external, time-dependent driving. In addition, nonconservative forces f_i could also be present. Each degree of freedom is coupled to a Langevin thermostat with damping constant γ_i , so that the general equations of motion read

$$\begin{aligned} \dot{q}_i &= \partial_{p_i} \mathcal{H} = \frac{p_i}{m_i} \equiv v_i, \\ \dot{p}_i &= -\partial_{q_i} \mathcal{H} + f_i - \gamma_i p_i + \xi_i. \end{aligned} \quad (2)$$

Here, the ξ_i represent Gaussian white noise with correlation $\langle \xi_i(t) \xi_j(t') \rangle = 2D_{ij} \delta(t - t')$. We first consider the case of independent heat baths in local equilibrium at temperature T_i , for which the fluctuation–dissipation theorem implies a diagonal diffusivity matrix $D_{ij} = m_i \gamma_i k_B T_i \delta_{ij}$. In section 6 we will show an example of a nondiagonal temperature matrix emerging for the normal modes of coupled oscillators. Note that a space-dependent noise is included in this formalism, since T_i may be a continuous function of the coordinates.

We use the formula for the time derivative of the average of any state observable $\mathcal{O}(t)$,

$$\frac{d}{dt} \langle \mathcal{O} \rangle = \langle \mathbb{L} \mathcal{O} \rangle, \quad (3)$$

where \mathbb{L} is the backward generator of the dynamics. For the Langevin equation (2) it can be derived with Itô's formula [10] and is given by

$$\mathbb{L} = \sum_{i=1}^{Nd} \left[\frac{p_i}{m_i} \partial_{q_i} + (f_i - \partial_{q_i} \mathcal{H} - \gamma_i p_i) \partial_{p_i} + \sum_{j=1}^{Nd} D_{ij} \partial_{p_i} \partial_{p_j} \right]. \quad (4)$$

A set of relations emerges immediately from the position–momentum observable⁸ $\mathcal{O} = p_i q_i$. Plugging it into (3), we obtain

$$\frac{d}{dt} \langle p_i q_i \rangle = \left\langle \frac{p_i^2}{m} \right\rangle + \langle (f_i - \partial_{q_i} \mathcal{H} - \gamma_i p_i) q_i \rangle. \quad (5)$$

Using then $\langle p_i q_i \rangle = m_i \langle \dot{q}_i q_i \rangle = \frac{1}{2} \frac{d}{dt} \langle m_i q_i^2 \rangle$ and removing all time derivatives by the assumption of stationarity, this is turned into a MVE for the conjugated pairs q_i, p_i :

$$\left\langle \frac{p_i^2}{m_i} \right\rangle = \langle (\partial_{q_i} \mathcal{H} - f_i) q_i \rangle. \quad (6)$$

The virial theorem follows by applying $\sum_{i=1}^{Nd}$ to both sides of (6). Notice that terms depending on the Langevin thermostat vanish and only mechanical forces survive in (6). Remarkably, (6) retains then the structure that one finds with the classic purely Hamiltonian derivation [1, 2]. As a counterexample, we address the Nosé–Hoover thermostats in section 7. The equipartition theorem is recovered in equilibrium ($f_i = 0, T_i = T \forall i$), where averages may be performed with the Boltzmann weight $\exp\left(-\frac{\mathcal{H}}{k_B T}\right)$ and all terms in (6) are equal to $k_B T$.

⁸ This derivation is formally identical to the one employed in most quantum mechanics textbooks, e.g. [11]. Indeed, $\langle \mathbb{L} \mathcal{O} \rangle = \langle \mathcal{O} \mathbb{W} \rangle = \langle \mathcal{O} \mathbb{W} - \mathbb{W} \mathcal{O} \rangle = \langle [\mathcal{O}, \mathbb{W}] \rangle$. This relation employs, in order, the definition of the generator of forward time evolution \mathbb{W} , the normalization of probabilities, and the definition of the commutator. The correspondence between \mathbb{W} and the quantum generator of time evolution $-\frac{i}{\hbar} \mathcal{H}$ then gives $\langle [\mathcal{O}, \mathbb{W}] \rangle = -\frac{i}{\hbar} \langle [\mathcal{O}, \mathcal{H}] \rangle$.

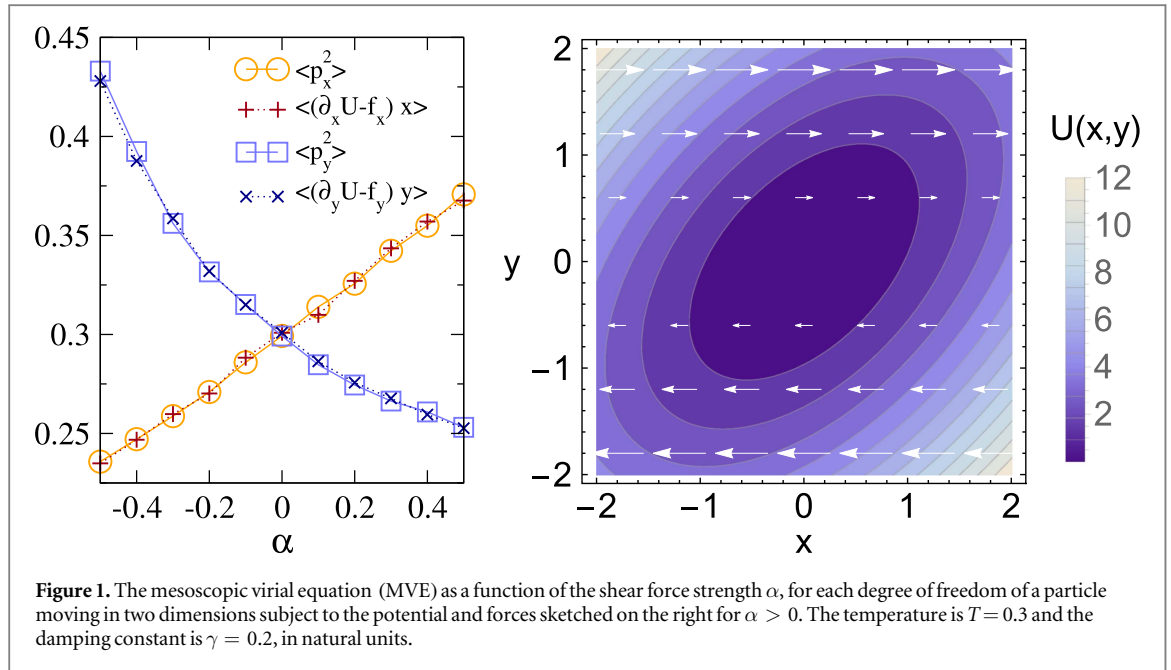


Figure 1. The mesoscopic virial equation (MVE) as a function of the shear force strength α , for each degree of freedom of a particle moving in two dimensions subject to the potential and forces sketched on the right for $\alpha > 0$. The temperature is $T = 0.3$ and the damping constant is $\gamma = 0.2$, in natural units.

As a basic exemplification, consider a unit-mass particle moving in the $\mathbf{q} = (x, y)$ plane, subjected to the potential $U(x, y) = x^2 - xy + y^2$ and to the nonconservative shear force $\mathbf{f} = \alpha y \mathbf{e}_x$ parallel to the x -axis unit vector \mathbf{e}_x . Throughout the text we employ α as a dimensional constant measuring the departure from equilibrium. In figure 1(a) we display a numerical validation of the MVE (6). Note that energy equipartition—with virial and (twice) kinetic contributions amounting to $k_B T$ —is achieved only in equilibrium (for $\alpha = 0$). This example also illustrates that the system acts as a toy refrigerator: specific degrees of freedom are cooled down under nonequilibrium conditions (for $\alpha \neq 0$) [12], despite energy being constantly supplied to the particle.

3. Generalised equations of state for steady nonequilibrium

Switching to the observable $\mathcal{O} = p_i^2$, equation (3) provides

$$\frac{d}{dt} \langle p_i^2 \rangle = 2 \langle (f_i - \partial_{q_i} \mathcal{H} - \gamma_i p_i) p_i \rangle + 2 \langle D_{ii} \rangle. \quad (7)$$

Here $\dot{Q}_i = \langle (f_i - \partial_{q_i} \mathcal{H}) \frac{p_i}{m_i} \rangle$ is recognised as the average heat flow into the i th reservoir, and in a steady state one gets the Harada–Sasa formula [13, 14]

$$\dot{Q}_i = \gamma_i \left(\left\langle \frac{p_i^2}{m_i} \right\rangle - k_B \langle T_i \rangle \right). \quad (8)$$

Combining now the MVE (6) with (8), we find

$$\frac{1}{\gamma_i} \dot{Q}_i + k_B \langle T_i \rangle = \langle (\partial_{q_i} \mathcal{H} - f_i) q_i \rangle. \quad (9)$$

If the system is in thermal equilibrium, then $\dot{Q}_i = 0 \forall i$, and (9) constitutes the starting point for deriving equations of state. Specifically, we recall the standard derivation of the mechanical one [15]. For interacting particles, labelled by $n = 1, \dots, N$ and having spatial coordinates \mathbf{r}_n within a container of volume \mathcal{V} , it is useful to separate the contribution of the external conservative forces \mathbf{F}_{ext} (comprising confining wall forces \mathbf{F}_w , gravity, etc) from that of the inter-particle interactions \mathbf{F}_{int} . The sum over all degrees of freedom of $\langle \partial_{q_i} \mathcal{H} q_i \rangle$ gives both the *internal* virial $C_{\text{int}} = -\sum_{i=1}^{Nd} \langle F_{\text{int},i} q_i \rangle$ [1] and the *external* virial $-\sum_{i=1}^{Nd} \langle F_{\text{ext},i} q_i \rangle$. The latter can be related to the pressure. Using the local particle density $\rho(\mathbf{r}) = \langle \sum_{n=1}^N \delta(\mathbf{r} - \mathbf{r}_n) \rangle$ we write

$$-\sum_{n=1}^N \langle \mathbf{F}_{\text{ext}}(\mathbf{r}_n) \cdot \mathbf{r}_n \rangle = -\int_{\mathcal{V}} d\mathbf{r} \mathbf{F}_{\text{ext}}(\mathbf{r}) \cdot \mathbf{r} \rho(\mathbf{r}). \quad (10)$$

Since the local stress tensor $\boldsymbol{\sigma}$ is defined by the steady-state equation expressing momentum conservation [15],

$$\nabla_{\mathbf{r}} \cdot \boldsymbol{\sigma}(\mathbf{r}) = \mathbf{F}_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \quad (11)$$

an integration by parts of (10) yields

$$-\sum_{i=1}^{Nd} \langle F_{\text{ext},i} q_i \rangle = \bar{P}_{\mathcal{V}} \mathcal{V} d. \quad (12)$$

Here the volume-averaged pressure $\bar{P}_{\mathcal{V}}$ is defined through the trace of the stress tensor $\bar{P}_{\mathcal{V}} \equiv \frac{1}{\mathcal{V}} \int_{\mathcal{V}} d\mathbf{r} \text{Tr} \boldsymbol{\sigma}(\mathbf{r})$. If the external force is just the confining force \mathbf{F}_w of the wall, the system clearly has a homogeneous pressure $\bar{P}_{\mathcal{V}} = P$. Under equilibrium conditions, from (9) thus descends

$$Nk_{\text{B}}T = P\mathcal{V} + C_{\text{int}}/d, \quad (13)$$

which can for example be used to derive the van der Waals equation [16].

The validity of (12) is not restricted to equilibrium systems, though. For simplicity, we may think about systems with equal particles and homogeneous dissipation ($T_i = T$ and $\gamma_i = \gamma \forall i$). The nonequilibrium stationary states are maintained, as in the case of figure 1(a), by the action of the nonconservative forces, which contribute the additional nonequilibrium virial term $C_{\text{ne}} \equiv -\sum_{i=1}^{Nd} \langle f_i q_i \rangle$ to (9). Two different cases should be distinguished, depending on the nature of f_i .

If f_i is an external driving, such as the shear force of section 2, C_{ne} combines with the conservative external forces in (11) to produce the pressure,

$$-\sum_{i=1}^{Nd} \langle (F_{\text{ext},i} + f_i) q_i \rangle = \bar{P}_{\mathcal{V}} \mathcal{V} d. \quad (14)$$

This can be easily shown noting that the momentum balance equation (11) under this nonequilibrium stationary condition becomes [17]

$$\nabla_{\mathbf{r}} \cdot \boldsymbol{\sigma}(\mathbf{r}) = (\mathbf{F}_{\text{ext}}(\mathbf{r}) + \mathbf{f}(\mathbf{r}))\rho(\mathbf{r}) - m\gamma\mathbf{u}(\mathbf{r})\rho(\mathbf{r}), \quad (15)$$

where $\mathbf{u}(\mathbf{r})\rho(\mathbf{r}) \equiv \langle \sum_{n=1}^N \mathbf{v}_n \delta(\mathbf{r} - \mathbf{r}_n) \rangle$ is the local particle current, which vanishes only at equilibrium (\mathbf{v}_n is the velocity of particle n). When integrated over the whole system, the additional friction term in (15) does not contribute to (12) thanks to the stationary continuity equation $\nabla_{\mathbf{r}} \cdot (\mathbf{u}\rho) = 0$, namely

$$\begin{aligned} -\sum_{n=1}^N \langle (\mathbf{F}_{\text{ext}}(\mathbf{r}_n) + \mathbf{f}(\mathbf{r}_n)) \cdot \mathbf{r}_n \rangle &= -\int_{\mathcal{V}} d\mathbf{r} (\nabla_{\mathbf{r}} \cdot \boldsymbol{\sigma}(\mathbf{r}) + m\gamma\mathbf{u}(\mathbf{r})\rho(\mathbf{r})) \cdot \mathbf{r} \\ &= \bar{P}_{\mathcal{V}} \mathcal{V} d + m\gamma \int_{\mathcal{V}} d\mathbf{r} \frac{r^2}{2} \nabla_{\mathbf{r}} \cdot (\mathbf{u}(\mathbf{r})\rho(\mathbf{r})) \\ &= \bar{P}_{\mathcal{V}} \mathcal{V} d. \end{aligned} \quad (16)$$

Hence the equation of state (13) is generalised to

$$\frac{1}{\gamma} \dot{Q} + Nk_{\text{B}}Td = \bar{P}_{\mathcal{V}} \mathcal{V} d + C_{\text{int}}, \quad (17)$$

where $\dot{Q} = \sum_i \dot{Q}_i$ is the mean rate of total heat dissipation into the reservoirs. Indeed, \dot{Q} is the constant housekeeping heat flux necessary to maintain the nonequilibrium stationary state.

If instead f_i is a dissipative interaction force between particles (e.g. describing binary inelastic collisions in granular gases [18]), then it is not present in (15), so that (12) holds true. As a result, the nonequilibrium virial C_{ne} figures explicitly in the generalised equation of state

$$\frac{1}{\gamma} \dot{Q} + Nk_{\text{B}}Td = \bar{P}_{\mathcal{V}} \mathcal{V} d + C_{\text{int}} + C_{\text{ne}}. \quad (18)$$

Interestingly, (17) and (18) include not only equilibrium thermodynamic variables but also the unusual average heat-flow $\dot{Q} = \langle \sum_i f_i \dot{q}_i \rangle$, which stems solely from the nonconservative driving because stationarity implies $\langle \sum_i \dot{q}_i \partial_{q_i} \mathcal{H} \rangle = \frac{d}{dt} \langle U \rangle = 0$. Mind the distinction between the steady state conditions addressed throughout the paper are distinct to path-dependent thermodynamics protocols. They are the reason why dissipative fluxes can be put on equal footing with state variables. We note that dissipative fluxes are upgraded to the status of state variables also in a phenomenological theory of extended irreversible thermodynamics [19].

As a simple illustration of the role of the mean heat flux, consider N independent particles with unitary mass, again in the xy -plane. Each particle is subjected to a Langevin bath of uniform temperature T , to a confining potential $U_w(x, y) = \frac{1}{12}(x^{12} + y^{12})$ so that $\mathbf{F}_w = -\nabla U_w$, and to an additional solid friction $\mathbf{f} = -\alpha \mathbf{v}/|\mathbf{v}|$ of constant magnitude $\alpha \geq 0$ [20, 21]. In the presence of this nonconservative friction, a steady state is generated in which heat is continuously taken from the Langevin bath and delivered to the substrate ($\dot{Q} < 0$). However, the symmetry of the problem implies that C_{ne} is zero. In view of the particles' mutual independency, also C_{int} is

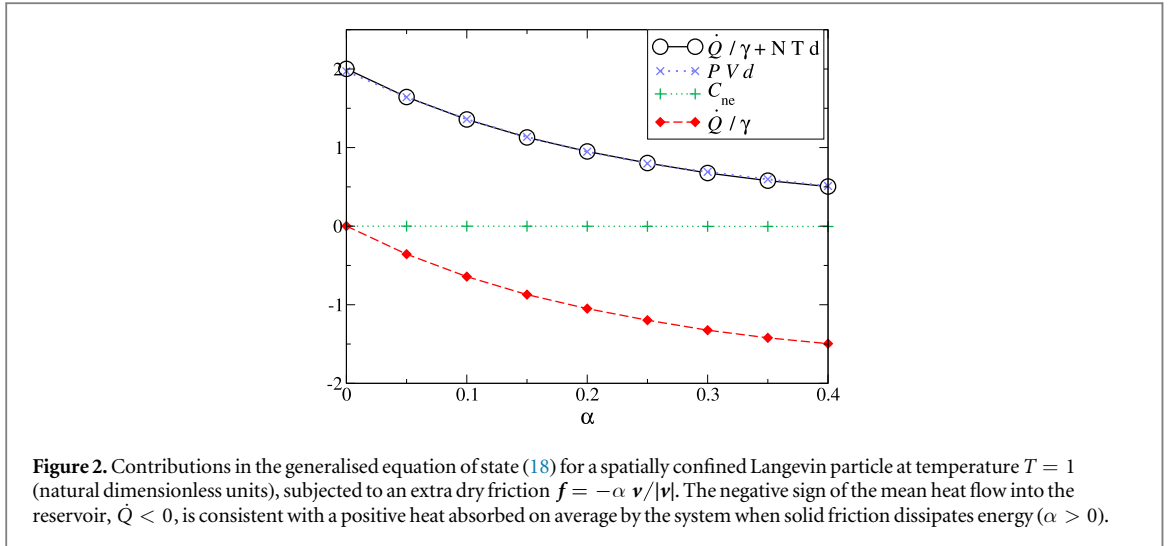


Figure 2. Contributions in the generalised equation of state (18) for a spatially confined Langevin particle at temperature $T = 1$ (natural dimensionless units), subjected to an extra dry friction $f = -\alpha \mathbf{v}/|\mathbf{v}|$. The negative sign of the mean heat flow into the reservoir, $\dot{Q} < 0$, is consistent with a positive heat absorbed on average by the system when solid friction dissipates energy ($\alpha > 0$).

exactly zero, and each of the remaining terms in (18) amounts to N times the single-particle contribution. In figure 2, we display each term in (18) as obtained from single-particle simulations for various α , finding $\dot{Q} = 0$ in equilibrium ($\alpha = 0$), while out of equilibrium \dot{Q} is negative and gives an important contribution that guarantees the validity of the generalised equation of state (18).

4. Overdamped dynamics

If one considers time scales much larger than the characteristic relaxation times of momenta, i.e. $\gamma_i dt \rightarrow \infty$ [10], then $\dot{Q}_i/\gamma_i \rightarrow 0$ and (9) reduces to the overdamped MVE⁹

$$k_B T_i = \left\langle \left(\frac{\partial U}{\partial q_i} - f_i \right) q_i \right\rangle. \quad (19)$$

This corresponds to (6) after the substitution $\langle p_i^2/m_i \rangle \mapsto k_B T_i$, as it should be expected, since momentum is instantaneously thermalised by its own thermal bath in the overdamped limit. Of course, this relation can be derived directly by taking the overdamped limit of the diffusion equation (2):

$$\dot{q}_i = \mu_i (-\partial_{q_i} U + f_i) + \hat{\xi}_i, \quad (20)$$

where $\mu_i = (m_i \gamma_i)^{-1}$ is the mobility, $\langle \hat{\xi}_i(t) \hat{\xi}_j(t') \rangle = 2\hat{D}_{ij} \delta(t - t')$ with $\hat{D}_{ij} = \mu_i k_B T_i \delta_{ij}$, and the Hamiltonian \mathcal{H} boils down to the potential energy U . The backward generator of the dynamics becomes $\mathbb{L} = \sum_i \mu_i (f_i - \partial_{q_i} U) \partial_{q_i} + \sum_{ij} \hat{D}_{ij} \partial_{q_i} \partial_{q_j}$, and $\mathcal{O} = q_i^2$ is the appropriate observable to plug in (3) to retrieve (19).

These results hold under the assumption that the dissipative force f_i acts effectively on time scales much longer than $1/\gamma_i$. If instead f_i is of order $O(\gamma_i)$, energy dissipation interferes with the thermalization process of momenta, so that $\langle p_i^2/m_i \rangle \neq k_B T_i$. For example, a solid friction (see section 3) of order $O(\alpha_i) \sim O(\gamma_i \sqrt{\langle p_i^2 \rangle})$ renders (8) in the form

$$\left\langle \frac{p_i^2}{2m_i} \right\rangle = k_B T_i - \frac{\alpha_i \sqrt{\langle p_i^2 \rangle}}{\gamma_i m_i}, \quad (21)$$

and thus yields an overdamped MVE which features nonequilibrium corrections to the bath temperature, of the form

$$k_B T_i - \frac{\alpha_i \sqrt{\langle p_i^2 \rangle}}{\gamma_i m_i} = \left\langle \left(\frac{\partial U}{\partial q_i} - f_i \right) q_i \right\rangle. \quad (22)$$

Active Brownian particles (see more details in the next section) can be taken as another example. In the overdamped limit, they are often modelled as colloidal particles driven by a propulsion force $f_{p,i}$ that is counterbalanced by an associated viscous drag force $-\alpha_i p_i$. Together they combine into the nonequilibrium force $f_i = -\alpha_i p_i + f_{p,i}$. If the friction forces are comparable in magnitude, that is $\alpha_i/\gamma_i = \text{const}$ in the limit

⁹To avoid the issues related to the interpretation of the overdamped stochastic equations hereafter we consider additive noise only.

$\gamma_i \rightarrow \infty$, equation (8) in the overdamped limit reads

$$\left\langle \frac{p_i^2}{2m_i} \right\rangle = \frac{k_B T_i}{1 + \frac{\alpha_i}{\gamma_i}}, \quad (23)$$

which implies a renormalised temperature for the overdamped MVE

$$\frac{k_B T_i}{1 + \frac{\alpha_i}{\gamma_i}} = \left\langle \left(\frac{\partial U}{\partial q_i} - f_i \right) q_i \right\rangle. \quad (24)$$

5. Overdamped active matter

Active Brownian particles are often employed as an overdamped model for the collective behaviour of motile bacteria and self-propelled colloids [22]. Their phase behaviour is currently much studied [9, 23–28]. In this regard, the utility of the virial theorem was pointed out in [27]. Here we fully exploit the generalised virial theorem and show how our approach leads to a pressure equation for active particles confined by hard walls of arbitrary geometry.

We describe an ensemble of identical active Brownian spheres moving in a two-dimensional volume \mathcal{V} in terms of their positions $\mathbf{r}_n = (x_n, y_n)$ and velocity orientations θ_n (hence, $\{\mathbf{q}_n\} = \{\mathbf{r}_n, \theta_n\}$). Their overdamped equations of motion are

$$\begin{aligned} \dot{\mathbf{r}}_n &= v_0 \mathbf{u}(\theta_n) + \mu \mathbf{F}_w(\mathbf{r}_n) + \sum_{m \neq n} \mu \mathbf{F}_{\text{int}}(\mathbf{r}_n - \mathbf{r}_m) + \hat{\xi}_n^{(r)}, \\ \dot{\theta}_n &= \hat{\xi}_n^{(\theta)}. \end{aligned} \quad (25)$$

The active velocity of modulus v_0 is directed along the unit vector $\mathbf{u}(\theta_n) = (\cos \theta_n, \sin \theta_n)$, and can be formally interpreted as another realization of the nonconservative force $\mathbf{f}_n = v_0 \mathbf{u}(\theta_n)/\mu$ that breaks detailed balance. Each particle experiences the others through the two-body force \mathbf{F}_{int} . No special symmetry is assumed for the confining hard walls acting via $\mathbf{F}_w(\mathbf{r}_n)$ at the container surface \mathcal{S} . The Gaussian translational noise $\hat{\xi}_n^{(r)}$ is characterised by $\langle \hat{\xi}_n^{(r)}(t) \hat{\xi}_m^{(r)}(t') \rangle = 2\mu k_B T \delta_{mn} \mathbf{1} \delta(t - t')$ and the Gaussian rotational noise $\hat{\xi}_n^{(\theta)}$ by $\langle \hat{\xi}_n^{(\theta)}(t) \hat{\xi}_m^{(\theta)}(t') \rangle = 2\hat{D}^{(\theta)} \delta_{mn} \delta(t - t')$. The backward generator \mathbb{L} is thus

$$\mathbb{L} = \sum_{n=1}^N \left[\left(v_0 \mathbf{u}(\theta_n) + \mu \mathbf{F}_w(\mathbf{r}_n) + \mu \sum_{m \neq n} \mathbf{F}_{\text{int}}(\mathbf{r}_n - \mathbf{r}_m) \right) \cdot \nabla_{\mathbf{r}_n} + \mu k_B T \nabla_{\mathbf{r}_n}^2 + \hat{D}^{(\theta)} \partial_{\theta_n}^2 \right], \quad (26)$$

and the choice of the observable $\mathcal{O} = \mathbf{r}_n^2$ in (3) yields the overdamped MVE

$$2k_B T = - \left\langle \left(\frac{1}{\mu} v_0 \mathbf{u}(\theta_n) + \mathbf{F}_w(\mathbf{r}_n) + \sum_{m \neq n} \mathbf{F}_{\text{int}}(\mathbf{r}_n - \mathbf{r}_m) \right) \cdot \mathbf{r}_n \right\rangle. \quad (27)$$

In the presence of activity one expects the pressure to be nonuniform due to particle aggregation at the boundaries [29–31] and phase separation [32], unless highly symmetric geometries are considered [9]. Note that in the momentum balance, which takes the form (11), the only external force is the wall interaction. Consistently with the assumption of a constant active speed v_0 , the self-propulsion force and the corresponding fluid friction balance each other and hence do not appear on the right hand side of (11).

For the special case of hard walls, we prove in the appendix that the external virial is proportional to the surface-averaged density $\bar{\rho}_S$, namely $-\sum_{n=1}^N \langle \mathbf{F}_w(\mathbf{r}_n) \cdot \mathbf{r}_n \rangle = 2\mathcal{V} k_B T \bar{\rho}_S$ [33, 34]. Moreover, inter-particle interactions do not contribute to the momentum flux across the wall, so that the surface-averaged pressure \bar{P}_S can only have a kinetic contribution [34, 35], $\bar{P}_S = k_B T \bar{\rho}_S$. The latter equilibrium result was recently rederived in the field of active matter [36]. It can be employed here since, in the overdamped description, momenta are assumed to be thermalised at the temperature T —by the choice of the translational noise's correlation. Therefore one arrives at the important result that the external virial gives the mean force per unit area exerted on the container

$$-\sum_{n=1}^N \langle \mathbf{F}_w(\mathbf{r}_n) \cdot \mathbf{r}_n \rangle = 2\bar{P}_S \mathcal{V}. \quad (28)$$

Combining (28) with the general result $-\sum_{n=1}^N \langle \mathbf{F}_w(\mathbf{r}_n) \cdot \mathbf{r}_n \rangle = 2\bar{P}_V \mathcal{V}$, which holds when \mathbf{F}_w is the only net external force acting on the system, we obtain the equality of average surface and volume pressure, $\bar{P}_S = \bar{P}_V$.

In the bulk, the interaction term in (27) gives a contribution analogous to the corrections to the ideal gas pressure in an equilibrium system. Indeed, for large N ,

$$\sum_{n,m \neq n} \langle \mathbf{F}_{\text{int}}(\mathbf{r}_n - \mathbf{r}_m) \cdot \mathbf{r}_n \rangle = -\frac{N^2}{2\mathcal{V}^2} \int_{\mathcal{V}} d\mathbf{r}' \int_{\mathcal{V}} d\mathbf{r}'' r \frac{\partial U_{\text{int}}}{\partial r} g(\mathbf{r}', \mathbf{r}''), \quad (29)$$

where $\mathbf{F}_{\text{int}} = -\nabla U_{\text{int}}$, $r \equiv |\mathbf{r}' - \mathbf{r}''|$, and g is the nonequilibrium pair density correlation function. In general, g cannot be reduced to a function of the relative pair position, since the system is inhomogeneous [37]. The explicit nonequilibrium contribution in (27) (the term containing v_0) gives rise to the so-called swim pressure [29, 32]. Using (3), this time with $\mathcal{O} = \mathbf{r}_n \cdot \mathbf{u}(\theta_n)$, and summing over n , we readily obtain

$$\begin{aligned} v_0 \hat{D}^{(\theta)} \sum_n \langle \mathbf{r}_n \cdot \mathbf{u}(\theta_n) \rangle &= Nv_0^2 + v_0 \mu \sum_n \langle \mathbf{F}_w(\mathbf{r}_n) \cdot \mathbf{u}(\theta_n) \rangle \\ &+ v_0 \mu \sum_{n,m \neq n} \langle \mathbf{F}_{\text{int}}(\mathbf{r}_n - \mathbf{r}_m) \cdot \mathbf{u}(\theta_n) \rangle. \end{aligned} \quad (30)$$

The first average on the right-hand side involves the particle polarization at the wall, while the second one represents the correlation between interactions and polarization. The constant term v_0^2 is an enhancement of the kinetic ‘ideal gas’ contribution due to the particles’ activity. Putting everything together, we obtain the generalised equation of state

$$\begin{aligned} \bar{P}_S \mathcal{V} &= Nk_B T - \frac{N^2}{4\mathcal{V}^2} \int_{\mathcal{V}} d\mathbf{r}' \int_{\mathcal{V}} d\mathbf{r}'' r \frac{\partial U_{\text{int}}}{\partial r} g(\mathbf{r}, \mathbf{r}') \\ &+ \frac{Nv_0^2}{2\mu \hat{D}^{(\theta)}} + \frac{v_0}{2\hat{D}^{(\theta)}} \sum_{n,m \neq n} \langle \mathbf{F}_{\text{int}}(\mathbf{r}_n - \mathbf{r}_m) \cdot \mathbf{u}(\theta_n) \rangle + \frac{v_0}{2\hat{D}^{(\theta)}} \sum_n \langle \mathbf{F}_w(\mathbf{r}_n) \cdot \mathbf{u}(\theta_n) \rangle. \end{aligned} \quad (31)$$

This result is valid irrespective of the confining geometry, thus extending the results of [27] and substantiating the numerical evidence for the equality of (average) wall and bulk pressure in large systems [29, 30]. Equation (31) is a mesoscopic generalised state equation that depends explicitly on the interaction with the wall through its last term. In equilibrium ($v_0 = 0$), the latter vanishes so that the pressure equation does not explicitly depend on \mathbf{F}_w , for every system size. Out of equilibrium, the thermodynamic limit ($N, \mathcal{V} \rightarrow \infty$ with N/\mathcal{V} constant) can be taken in order to get rid of this surface term, which is a peculiarity of torque-free active Brownian particles with constant self-propulsion. When aligning interactions are added into the model, the active particle pressure appears to depend explicitly on the interactions with the boundaries and not only on thermodynamic properties (temperature, density, etc) [25]. Of course, the framework based on the MVE is unaffected by such dynamical details and can be applied even to models qualitatively different from (25) (see [38]).

6. Normal modes of coupled oscillators

The derivation of the MVE does not rely on the diagonality of the matrix D_{ij} , that is (6) also holds for systems in which the noise components are cross-correlated. An instance of such a situation is offered by the analysis of the normal modes of a system with local reservoirs. For harmonic lattices [7], depending on the details of the forcing and on boundary conditions, the energy stored in long wavelength vibrational modes may be either enhanced or reduced compared to the average. Here, we illustrate the MVE in modes’ space for a one-dimensional chain of N point masses coupled with quadratic–quartic interactions, thus going beyond the harmonic approximation. The stochastic equation of the normal modes, obtained by applying a linear transformation to the equation (2) for the oscillators’ position and velocity [39], is

$$\ddot{X}_k = -\gamma \dot{X}_k - \omega_k^2 X_k - \epsilon \sum_{l,r,s} \mathcal{B}_{klrs} X_l X_r X_s + \eta_k, \quad (32)$$

where ω_k^2 is the squared eigenfrequency of the k th mode and $\epsilon \mathcal{B}_{klrs}$ is a tensor that emerges from the quartic interactions. The noise terms η_k are mutually correlated according to

$$\langle \eta_k(t) \eta_l(t') \rangle = 2\gamma k_B \mathcal{T}_{kl} \delta(t - t'). \quad (33)$$

The symmetric matrix \mathcal{T}_{kl} of mode temperatures [12], is in general not diagonal unless the system is in equilibrium.

Without the anharmonic coupling, $\epsilon = 0$, the average kinetic and potential energy of the modes satisfy

$$\langle \dot{X}_k^2 \rangle = \omega_k^2 \langle X_k^2 \rangle = k_B \mathcal{T}_{kk}, \quad (34)$$

where the first equality is analogous to (6), and the second amounts to (9) specialised to the present analysis. Notice that the kinetic and potential energy coincide for a given mode, but differ in general for different modes, thus breaking full equipartition. With $\epsilon \neq 0$ the modes’ dynamics is coupled via the tensor \mathcal{B}_{klrs} and the MVE (6) becomes

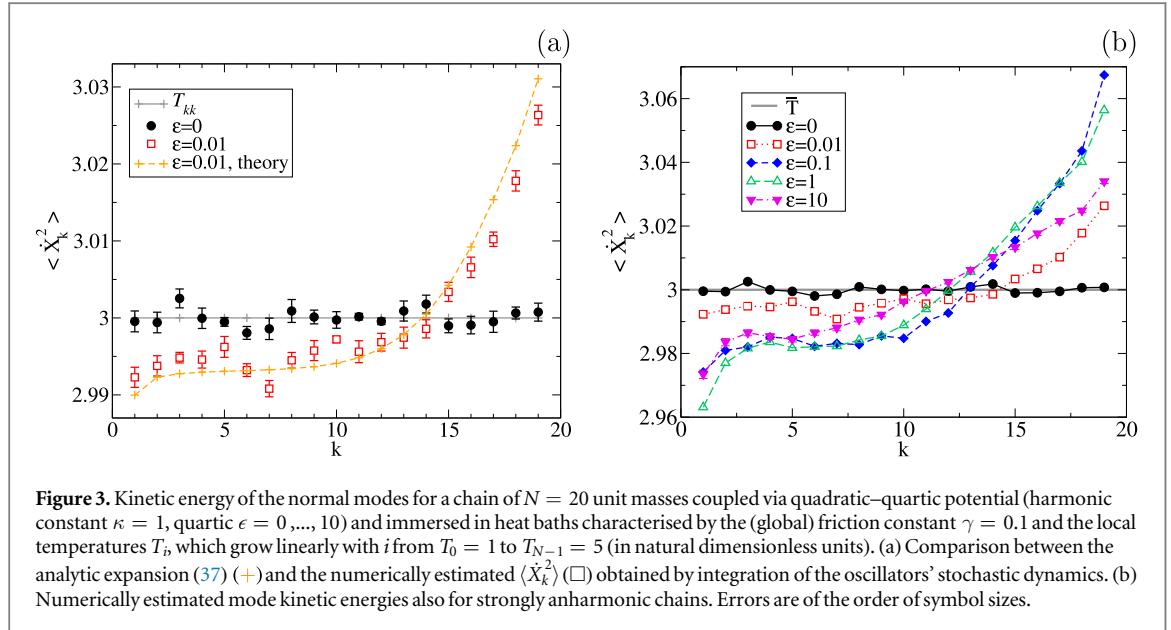


Figure 3. Kinetic energy of the normal modes for a chain of $N = 20$ unit masses coupled via quadratic–quartic potential (harmonic constant $\kappa = 1$, quartic $\epsilon = 0, \dots, 10$) and immersed in heat baths characterised by the (global) friction constant $\gamma = 0.1$ and the local temperatures T_i , which grow linearly with i from $T_0 = 1$ to $T_{N-1} = 5$ (in natural dimensionless units). (a) Comparison between the analytic expansion (37) (+) and the numerically estimated $\langle \dot{X}_k^2 \rangle$ (\square) obtained by integration of the oscillators’ stochastic dynamics. (b) Numerically estimated mode kinetic energies also for strongly anharmonic chains. Errors are of the order of symbol sizes.

$$\langle \dot{X}_k^2 \rangle = \omega_k^2 \langle X_k^2 \rangle + \epsilon \sum_{l,r,s} \mathcal{B}_{klrs} \langle X_k X_l X_r X_s \rangle \quad (35)$$

containing no explicit sign of the nondiagonal \mathcal{T}_{kl} , as anticipated above. Similarly, the heat-flux equation (8) becomes

$$\langle \dot{X}_k^2 \rangle = k_B \mathcal{T}_{kk} + \frac{\epsilon}{\gamma} \sum_{l,r,s} \mathcal{B}_{klrs} \langle \dot{X}_k X_l X_r X_s \rangle. \quad (36)$$

This represents the perfect starting point for studying perturbative corrections to mode energies, given the Gaussian statistics of the X_k ’s for $\epsilon = 0$. In equilibrium ($T_i = T \forall i$), where the modes’ position and velocity are on average uncorrelated, the last term disappears, so that (36) implies the equipartition for velocities $\langle \dot{X}_k^2 \rangle = k_B T$. Under nonequilibrium conditions, the nonzero heat flux modifies the mode kinetic energy in (36). For small ϵ we can expand (36) as

$$\langle \dot{X}_k^2 \rangle = k_B \mathcal{T}_{kk} + \frac{3\epsilon}{\gamma} \sum_{l,r,s} \mathcal{B}_{klrs} \langle \dot{X}_k X_l \rangle_{\epsilon=0} \langle X_r X_s \rangle_{\epsilon=0} + O(\epsilon^2). \quad (37)$$

Here we used the symmetry of the tensor \mathcal{B} together with Wick’s theorem to break up the Gaussian correlations $\langle \dots \rangle_{\epsilon=0}$ evaluated in the harmonic system [12].

An illustration of (37) is provided in figure 3(a) for a one-dimensional lattice with fixed boundaries immersed in a linear temperature profile. For purely harmonic couplings ($\epsilon = 0$), the modes enjoy a peculiar full energy equipartition [12] at the average temperature $\mathcal{T}_{kk} = \bar{T} \equiv \frac{1}{N} \sum_{i=0}^{N-1} T_i$, which is due to the symmetry in the T_i ’s and in the boundary conditions. The anharmonic terms allow energy to leak into the higher, more localised modes. The same qualitative behaviour is found numerically for increasing values of ϵ (figure 3(b)). The energy repartition among modes is thus robust against the introduction of nonlinearities and fairly well approximated by a first order perturbative calculation. Note that the total kinetic energy is insensitive to ϵ , namely $\sum_{k=0}^{N-1} \langle \dot{X}_k^2 \rangle = k_B \sum_{k=0}^{N-1} \mathcal{T}_{kk} \forall \epsilon$, since the total flux appearing in (36) sum up to zero under stationary conditions, thanks to the potential nature of the interaction:

$$\sum_{k,l,r,s} \mathcal{B}_{klrs} \langle \dot{X}_k X_l X_r X_s \rangle = \sum_{k=0}^{N-1} \langle \dot{X}_k (\partial_k U - \omega_k^2 X_k) \rangle = \frac{d}{dt} \left(\langle U \rangle - \sum_{k=0}^{N-1} \frac{\omega_k^2}{2} \langle X_k^2 \rangle \right) = 0. \quad (38)$$

7. Deterministic thermostats

The relations derived above for stochastic inertial systems remain valid in the zero-noise limit, where the dynamics becomes deterministic. Stationarity is then ensured by coupling the system to suitably defined thermostats. Examples are Nosé–Hoover thermostats, where extra degrees of freedom act as frictional couplings for the physical ones [40]. Similarly to Langevin dynamics, they guarantee canonical thermalization in cases of uniform temperatures, and they lead to nonzero heat fluxes if different temperatures are imposed on different degrees of freedom of the system. For lattices of oscillators interacting only via conservative forces and coupled

to Nosé–Hoover thermostats at various temperatures, the existence of local energy equipartition is a common assumption needed for the local definition of temperature [41]. So far, it has only been observed in simulations for the masses not directly driven by Nosé–Hoover thermostats [42]. Here we provide a formal proof. We consider statistical averages with respect to the invariant density, which, in general, may or may not coincide with time averages. Equality is assured by the use of Nosé–Hoover chains of thermostats [43].

The Nosé–Hoover dynamics for unit masses is given by

$$\dot{q}_i = p_i, \quad \dot{p}_i = -\partial_{q_i} U - \Theta_i \zeta_i p_i, \quad \dot{\zeta}_i = \frac{1}{\tau^2} \left(\frac{p_i^2}{k_B T_i} - 1 \right), \quad (39)$$

where Θ_i is an indicator function, which is 1 or 0 depending on whether the mass i is coupled or not to a thermostat. The auxiliary feedback variable ζ_i aims at thermalizing p_i at the temperature T_i on a timescale τ . The backward generator associated to (39) is

$$\mathbb{L} = \sum_{i=1}^{Nd} \left\{ p_i \partial_{q_i} - \partial_{q_i} U \partial_{p_i} + \Theta_i \left[-\zeta_i p_i \partial_{p_i} + \frac{1}{\tau^2} \left(\frac{p_i^2}{k_B T_i} - 1 \right) \partial_{\zeta_i} \right] \right\}.$$

Following the scheme outlined above, we find the generalised MVE

$$\langle p_i^2 \rangle = \langle q_i \partial_{q_i} U \rangle + \Theta_i \langle \zeta_i p_i q_i \rangle, \quad (40)$$

which includes the formal justification for the mentioned numerical observation of local energy equipartition if restricted to masses without a local thermostat [42], corresponding to $\Theta_i = 0$. The term

$$\langle \zeta_i p_i q_i \rangle = -\frac{1}{2\tau^2} \left\langle \left(\frac{p_i^2}{k_B T_i} - 1 \right) q_i^2 \right\rangle, \quad (41)$$

stemming from the thermostat's force (that can be seen as another realization of the nonconservative force f_i), is identically zero in equilibrium, where momentum and position are uncorrelated and $\langle p_i^2 \rangle = k_B T_i$ holds also for the degrees of freedom coupled to thermostats.

8. Conclusions

For a wide class of nonequilibrium systems in steady states, including stochastic and deterministic thermostated dynamics, we have shown that the kinetic energy of a given degree of freedom is on average equal to the corresponding virial of the forces. An integration over all degrees of freedom of such MVE yields the standard (macroscopic) virial theorem and a variety of useful results for general nonequilibrium systems. It is indeed possible to follow the path valid for equilibrium systems, using the virial theorem as a tool for the derivation of generalised equations of state that involve pressure, temperature and other observables. For inertial systems with dissipative dynamics, this leads to an intriguing relation between the virial, the temperature of the heat baths, and the heat flux into them. Similarly, for active Brownian particles a generalised equation of state valid for arbitrary container geometries ensues. A direct experimental verification of the fundamental mesoscopic virial relations (underlying all these results) would therefore be desirable. In boundary driven systems with conservative internal forces, such verification amounts to checking energy equipartition between momentum–position type conjugate variables.

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Appendix. Pressure on a hard wall

In section 5 we argued that the external virial given by the a hard wall force is proportional to the pressure averaged over the wall surface. To prove this point, we basically collect and repeat the arguments of [33, 34], as they assume stationarity and require the particle momenta to be thermalised to the bath temperature T , only. For the local stress tensor σ this leads to the splitting

$$\nabla_r \cdot \sigma = k_B T \nabla_r \rho + \nabla_r \cdot \sigma_{\text{int}}. \quad (\text{A.1})$$

Recall that $\boldsymbol{\sigma}(\mathbf{r})$ gives the momentum exchanged across a surface placed in \mathbf{r} . Hence, the two terms on the right-hand side of (A.1) represent, respectively, the momentum transferred kinetically by particles crossing the surface and the momentum exchanged between particles separated by the surface itself. Using (A.1), multiplying the momentum balance equation (15) (with $f=0$) by \mathbf{r} and integrating over \mathcal{V}_- , defined as an inner volume infinitesimally smaller than \mathcal{V} , yields

$$\int_{\mathcal{V}_-} d\vec{r} (\nabla_r \cdot \boldsymbol{\sigma}_{\text{int}}) \cdot \mathbf{r} + m\gamma \int_{\mathcal{V}_-} d\vec{r} \mathbf{u} \rho \cdot \mathbf{r} = dk_B T (\bar{\rho}_V - \bar{\rho}_S). \quad (\text{A.2})$$

Here we have used that $\mathbf{F}_w(\mathbf{r}) = 0$ for $\mathbf{r} \in \mathcal{V}_-$, and \mathcal{S} indicates the surface of \mathcal{V}_- . On the other hand, using that the particle density vanishes identically on the hard wall, an integration over the whole system gives

$$\int_{\mathcal{V}} d\vec{r} (\nabla_r \cdot \boldsymbol{\sigma}_{\text{int}}) \cdot \mathbf{r} + m\gamma \int_{\mathcal{V}} d\vec{r} \mathbf{u} \rho \cdot \mathbf{r} = \int_{\mathcal{V}} d\vec{r} \mathbf{F}_w \rho \cdot \mathbf{r} + dk_B T \bar{\rho}_V. \quad (\text{A.3})$$

The left-hand side of (A.2) and (A.3) are equal, since the integrands are finite everywhere in the system and the integration domains only differ in a set of zero measure. Hence, we conclude that the external virial for hard walls is only proportional to the surface averaged density

$$-\sum_{n=1}^N \langle \mathbf{F}_w(\mathbf{r}_n) \cdot \mathbf{r}_n \rangle = 2\mathcal{V} k_B T \bar{\rho}_S. \quad (\text{A.4})$$

Then, one applies the rationale behind (A.1) to the momentum exchanged at the wall, which is by definition the surface averaged pressure \bar{P}_S . Namely, it may consist of the kinetic contribution $k_B T \bar{\rho}_S$ and a configurational term coming from inter-particle interactions. Yet, the latter is identically zero on a hard wall, since no configuration is allowed with particles on both side of the wall surface. Therefore, plugging $\bar{P}_S = k_B T \bar{\rho}_S$ into (A.4), we arrive at the sought result (28).

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Energy repartition for a harmonic chain with local reservoirsGianmaria Falasco,^{1,*} Marco Baiesi,^{2,3} Leo Molinaro,² Livia Conti,³ and Fulvio Baldovin^{2,3,4,†}¹*Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, D-04009 Leipzig, Germany*²*Department of Physics and Astronomy, University of Padova, Via Marzolo 8, I-35131 Padova, Italy*³*INFN, Sezione di Padova, Via Marzolo 8, I-35131 Padova, Italy*⁴*Sezione CNISM Università di Padova, Via Marzolo 8, I-35131 Padova, Italy*

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We exactly analyze the vibrational properties of a chain of harmonic oscillators in contact with local Langevin heat baths. Nonequilibrium steady-state fluctuations are found to be described by a set of mode temperatures, independent of the strengths of both the harmonic interaction and the viscous damping. Energy is equally distributed between the conjugate variables of a given mode but differently among different modes, in a manner which depends exclusively on the bath temperatures and on the boundary conditions. We outline how bath-temperature profiles can be designed to enhance or reduce fluctuations at specific frequencies in the power spectrum of the chain length.

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I. INTRODUCTION

The enhancement of nonequilibrium fluctuations at low wave numbers is a key feature of systems driven by thermodynamic gradients (see [1] for a review). For temperature gradients, it has been thoroughly studied both theoretically [2], and experimentally in systems ranging from simple fluids [3] to polymer solutions [4] and fluid layers also under the influence of gravity [5]. More recently, fluctuations in nonisothermal solids have been the subject of experimental investigation, fostered by the possibility of technological applications in fields as diverse as microcantilever-based sensors [6] and gravitational wave detectors [7]. For example, the low frequency vibrations of a metal bar, whose ends are set at different temperatures, were found to be larger than those predicted by the equipartition theorem at the local temperature [8], thus corroborating the generality of the results obtained for nonequilibrium fluids [9]. (See also experiments with cantilevers [10].)

Theoretical studies of nonequilibrium solids focused more on thermal conduction in low dimensions, where crystals are usually modeled as Fermi-Pasta-Ulam oscillator chains coupled at the boundaries with heat baths at different temperatures [11–13]. Thanks to their simplicity, integrable and quasi-integrable models may be taken as a paradigm to describe more comprehensively the energetics of normal solids under nonisothermal conditions. For instance, anomalous features are known to disappear when, in place of nonhomogeneous boundary conditions at the borders, a temperature gradient is generated by stochastic heat baths displaced along the system [13]. Specifically, it has been shown that self-consistent heat baths—such that no energy flows on average into or out of the reservoirs—are sufficient to recover the Fourier’s law of heat conduction in a harmonic chain [14–16]. Lifting the “self-consistency” condition, one obtains a simple, yet general, model which describes a solid immersed in a locally equilibrated medium [17–19]. This can find application in all

cases where the study of fluctuations is applied to an extended system with a complex thermal balance. As an example, we may cite cryogenic gravitational wave detectors, where thermal fluctuations of the systems composed by the test masses and their multistage suspension chains are of central importance. The latter are effectively coupled to different heat baths and flows [20].

Here we analyze the energy repartition among the elastic modes of a harmonic chain held in temperature gradient, as sketched in Fig. 1(a). In a coarse-grained picture, the oscillator displacements can be thought of as the local strain of a (one-dimensional) elastic dispersive body, such that the model describes the damped propagation of thermal phonons [Fig. 1(b)]. Our approach is fully analytic and provides an explicit expression for the energy repartition among the modes in terms of their effective temperatures \mathcal{T}_{kk} . Exemplifying our results for temperature profiles with a defined concavity, we show that \mathcal{T}_{kk} ’s depend only on this concavity and on the boundary conditions of the system. A naive expectation could be that deviations from energy equipartition are to be anticipated at long wavelengths only, since local equilibrium conditions should hold at short scales. On the contrary, we find that both long and short wavelength modes can either heat up or cool down well beyond the average temperature. We also study a reverse-engineering approach in which the heat bath temperatures are inferred starting from a desired energy repartition.

II. MODEL AND GENERAL RESULTS

Consider a linear chain of $N + 1$ equal oscillators located at positions q_n ($n = 0, 1, \dots, N$). Successive masses are connected through a harmonic potential of equilibrium length l_0 . Each of them is in contact with a specific Langevin bath at temperature T_n [21], providing viscous damping with coefficient γ and thermal noise ξ_n . Setting masses to unity, the equations of motion in the displacement coordinate $R_n \equiv q_n - n l_0$ read

$$\ddot{R}_n = -\gamma \dot{R}_n - \kappa \sum_{m=0}^N A_{nm} R_m + \xi_n, \quad (1)$$

*falasco@itp.uni-leipzig.de

†baldovin@pd.infn.it

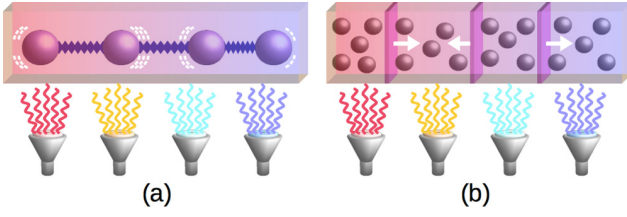


FIG. 1. (Color online) (a) Sketch of the linear chain of N harmonic oscillators held in a temperature gradient: each oscillator is coupled to an independent heat bath at temperature T_n , $n = 0, \dots, N$ (in the picture $N = 3$). (b) Schematic interpretation in terms of sound propagation in a medium.

where A_{nm} is a tridiagonal matrix accounting for first-neighbors interactions via the potential $\frac{\kappa}{2}(R_m - R_{m-1})^2$. In Eq. (1) the standard Gaussian white noise ξ_n has an amplitude given by the fluctuation-dissipation theorem at the local temperature (in units of k_B):

$$\langle \xi_m(t) \xi_n(t') \rangle = 2\gamma T_n \delta(t - t') \delta_{mn}. \quad (2)$$

In the following, we first consider the case of free boundary conditions ($A_{00} = A_{NN} = 1$); fixed ($A_{00} = A_{NN} = 0$) and mixed ($A_{00} = 1, A_{NN} = 0$) boundary conditions are discussed in Sec. III and in Appendix A. With free boundaries the matrix A_{nm} is diagonalized by the linear transformation $\Phi^{-1}A\Phi$, with

$$\Phi_{kn}^{-1} = \frac{1}{N+1} \cos\left(\frac{k\pi}{N+1}\left(n + \frac{1}{2}\right)\right), \quad (3)$$

mapping the spatial coordinates R_n into the coordinates of the normal modes $X_k \equiv \sum_n \Phi_{kn}^{-1} R_n$, for which

$$\ddot{X}_k = -\gamma \dot{X}_k - \omega_k^2 X_k + \eta_k, \quad (4)$$

where $\omega_k^2 = 4\kappa \sin^2\left(\frac{k\pi}{2(N+1)}\right)$ is the (squared) eigenfrequency of the k th mode. In this dynamics, the only source of correlation between modes is contained in the transformed Gaussian white noises $\eta_k \equiv \sum_n \Phi_{kn}^{-1} \xi_n$,

$$\langle \eta_k(t) \eta_{k'}(t') \rangle = 2\gamma \mathcal{T}_{kk'} \delta(t - t') / (N+1). \quad (5)$$

These correlations include a ‘‘temperature’’ matrix

$$\mathcal{T}_{kk'} \equiv (N+1) \sum_{n=0}^N \Phi_{kn}^{-1} \Phi_{k'n}^{-1} T_n, \quad (6)$$

which is certainly diagonal only in the equilibrium case $T_n = T \forall n$, where energy equipartition is recovered. In a nonequilibrium state, generated by heterogeneous bath temperatures, the diagonal \mathcal{T}_{kk} still encodes information about how energy is distributed among the modes. Nonzero off-diagonal $\mathcal{T}_{kk'}$ emerge in connection with energy fluxes. To show this, we consider the average kinetic energy (K_k) and potential energy (V_k) of the k th mode,

$$K_k \equiv (N+1) \langle \dot{X}_k^2 \rangle (1 - \delta_{k0}/2), \quad V_k \equiv (N+1) \omega_k^2 \langle X_k^2 \rangle,$$

where expectation values $\langle \cdot \rangle$ are taken over different realizations of the thermal noise ξ_n . We get the variances $\langle X_k^2 \rangle, \langle \dot{X}_k^2 \rangle$

from the solution of Eq. (4) (Appendix B),

$$X_k(t) = \sum_{\alpha=1,2} \int_{-\infty}^t dt' \frac{(-1)^\alpha}{\lambda_k^\alpha - \lambda_k} e^{-\lambda_k^\alpha(t-t')} \eta_k(t'), \quad (7)$$

where $\lambda_k^{(\alpha)}$ with $\alpha = 1, 2$ are the roots of the characteristic equation for the unforced harmonic oscillator; namely, $\lambda_k^{(\alpha)} = -\frac{1}{2}[\gamma + (-1)^\alpha \sqrt{\gamma^2 - 4\omega_k^2}]$. For each mode k , both the average kinetic and potential energy turn out to coincide with one half of the mode temperature (Appendix B):

$$K_k^X = V_k^X = \mathcal{T}_{kk}/2 \quad (k \neq 0). \quad (8)$$

This relation establishes a form of energy equipartition between the conjugate variables of a single mode. Interestingly, from (6) and (3) one sees that \mathcal{T}_{kk} does not depend on the details of both the harmonic interaction (κ) and the damping (γ). Therefore, the amount of energy stored in the k th mode is directly determined by the choice of the bath temperature profile T_n , for given boundary conditions. Put in other words, properly designing thermal profiles it is in principle possible to enhance or reduce the thermal vibrations of specific modes. All these findings are confirmed by numerical integration of Eq. (1).

III. ROLE OF THE BOUNDARY CONDITIONS

In the case of free boundaries, Eq. (6) gives

$$\mathcal{T}_{kk} = \bar{T} \left[1 + \frac{\sum_{n=0}^N T_n \cos\left(\frac{2n+1}{N+1}k\pi\right)}{\sum_{m=0}^N T_m} \right] \quad (k \neq 0), \quad (9)$$

where $\bar{T} \equiv \sum_{n=0}^N T_n / (N+1)$ is the average imposed temperature. The center-of-mass kinetic energy $(N+1)\langle \dot{X}_0^2 \rangle / 2$ is equal to $\mathcal{T}_{00} = \bar{T}$. Notice that Eq. (9) is valid in particular when T_n corresponds to a self-consistent profile [14–16]. In (9) the energy stored by the mode k under stationary nonequilibrium conditions emerges like a correction to the average temperature \bar{T} , which at most amounts to $\pm \bar{T}$. This correction can be viewed as a weighted average of a cosine function over the temperature profile: For parity, it vanishes for all temperature profiles which are odd with respect to $(N/2, \bar{T})$. The relevant physical consequence is that with free boundary conditions energy equipartition is extended to all nonequilibrium temperature profiles which are odd symmetric with respect to $(N/2, \bar{T})$, like linear profiles. At variance, if the temperature profile has a definite upwards (downwards) concavity in the interval $[0, N]$, low- (high-) k modes heat up and high- (low-) k modes freeze down. We exemplify these findings assuming heat-bath temperatures $T_n = T_0 + (n/N)^\alpha (T_N - T_0)$ with $T_0 = 10, T_N = 1$, and $N = 99$ (see Fig. 2): $\alpha = 1$ corresponds to a linear temperature profile, whereas $\alpha < 1$ ($\alpha > 1$) corresponds to a profile with upwards (downwards) concavity. In Fig. 3(a) one finds the resulting \mathcal{T}_{kk} for free boundary conditions.

Transport properties might depend crucially on the boundary conditions [22]. We show that the latter strongly influences also the repartition of energy among the normal modes. For

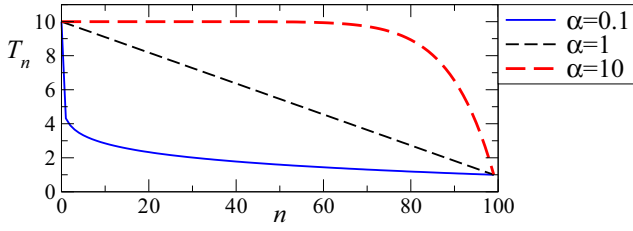


FIG. 2. (Color online) Heat-bath profiles utilized for exemplifying our results.

fixed boundary conditions, \mathcal{T}_{kk} becomes (Appendix A)

$$\mathcal{T}_{kk} = \frac{(N-1)\bar{T}}{N} \left[1 - \frac{\sum_{n=1}^{N-1} T_n \cos\left(\frac{2nk}{N}\pi\right)}{\sum_{m=1}^{N-1} T_m} \right] \quad (10)$$

($0 < k < N$), with $\bar{T} \equiv \sum_{n=1}^{N-1} T_n / (N-1)$. Figure 3(b) shows the mode energy repartition for the same profiles T_n used for open boundary conditions in Fig. 3(a). Notably, the low- k behavior is inverted. For instance, while free boundaries

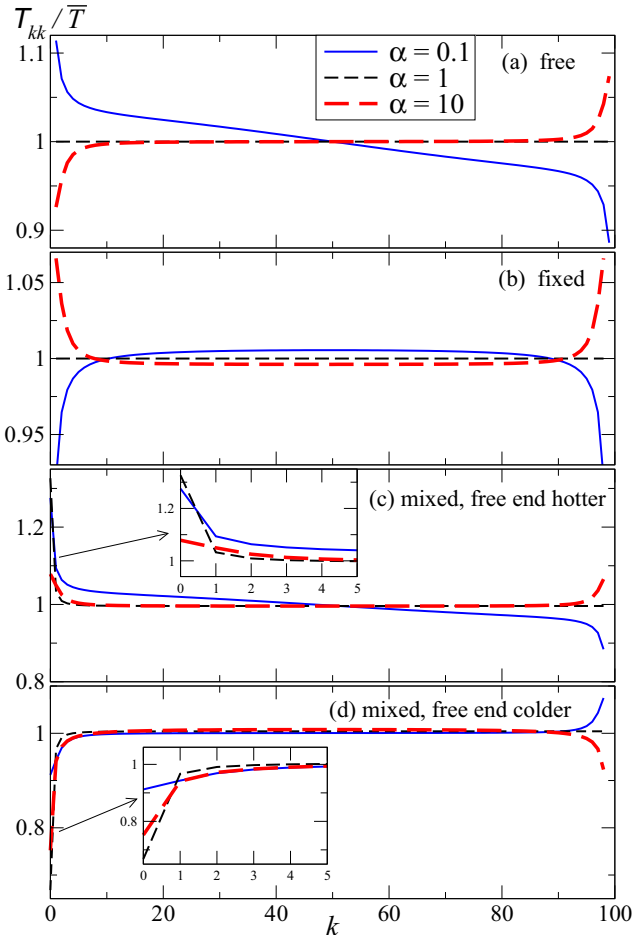


FIG. 3. (Color online) Modes normalized temperatures \mathcal{T}_{kk}/\bar{T} calculated through Eqs. (9), (10), and (11) for the heat-bath profiles mentioned earlier. The four panels refer to different boundary conditions: (a) free, (b) fixed, (c) mixed with free end hotter than the fixed end, and (d) vice versa. Insets enlarge the plots at low k 's.

enhance the long-wavelength energy storage for concave-up T_n , fixed boundaries do the opposite. Hence, if the aim were to store energy at low k 's, a convenient strategy would be to heat up the boundaries and cool down the middle of a free chain, and vice versa with a fixed chain.

For mixed boundaries in which we leave free the mass at $n = 0$ and fix the mass at $n = N$ we have (Appendix A)

$$\mathcal{T}_{kk} = \frac{2N\bar{T}}{2N+1} \left[1 + \frac{\sum_{n=0}^{N-1} T_n \cos\left(\frac{(2n+1)(2k+1)\pi}{2N+1}\right)}{\sum_{m=0}^{N-1} T_m} \right] \quad (11)$$

($k < N$), with $\bar{T} \equiv \sum_{n=0}^{N-1} T_n / N$. Due to the broken symmetry upon profile reflection with respect to the vertical axis passing through $N/2$, in our exemplification we may distinguish two cases for each temperature profile: one in which the hotter temperatures are applied at the side of the free end in $n = 0$ (as in Fig. 2) and one in which hot temperatures are applied at the side of the fixed mass in $n = N$ (perform the transformation $T_n \mapsto T_{N-n}$ to the profiles in Fig. 2). Results are respectively depicted in Figs. 3(c) and 3(d). In both cases, even the linear temperature profile does not lead to equipartition. From the plots one notices that low- k modes store more energy if the free end is hotter. This alludes to suggestive implications: the mixed boundary is the case considered in Ref. [8], where an experiment with a solid bar and a numerical study of an anharmonic chain displayed behaviors qualitatively consistent with that of Fig. 3(c). Our results thus suggest that the noise at lowest k 's would be lowered by letting the free end float in a colder environment. This also points out a conceivable indication for reducing the measured thermal noise in experiments possible to schematizations analogous to those in Fig. 1.

IV. REVERSE ENGINEERING

The expression $\mathcal{T}_{kk}(T_n)$ may be inverted, thus determining which heat-bath temperature profiles T_n may correspond to a given mode energy repartition. For definiteness, let us focus on the case of free boundaries. Thanks to simple identities (Appendix C), the inversion of Eq. (9) gives

$$T_n + T_{N-n} = 2 \sum_{k=1}^N \cos\left(\frac{2n+1}{N+1}k\pi\right) \mathcal{T}_{kk} + 2\bar{T}. \quad (12)$$

Notice that, given \mathcal{T}_{kk} , the temperature profile T_n is not uniquely identified. In fact, the relation $\mathcal{T}_{kk}(T_n)$ is many-to-one—for instance, already on the basis of symmetry one can figure out that temperature profiles T_n , T'_n related by the transformation $T'_n = T_{N-n}$ produce the same energy repartition \mathcal{T}_{kk} . In the lower panel of Fig. 4 we display a profile reconstruction originated from the specific choice for \mathcal{T}_{kk} reported in the upper one. For simplicity, we complemented Eq. (12) with the condition $T_n = T_{N-n}$; this means, in particular, $T_0 = T_N$. Our example points out that in principle it is possible to design heat-bath temperature profiles so that the energy stored in the normal modes of the chain is arbitrarily distributed in the range $[0, 2\bar{T}]$, consistently with the condition $\sum_{k=1}^N \mathcal{T}_{kk} = N\bar{T}$.

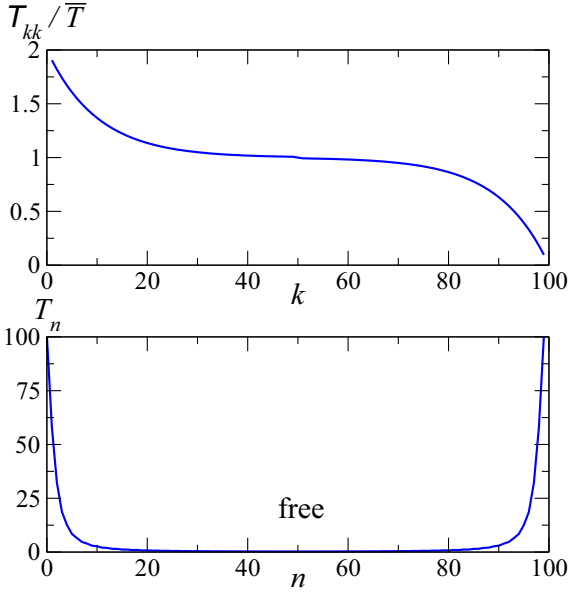


FIG. 4. (Color online) Reconstruction of the temperature profile (lower panel) through Eq. (12), starting from T_{kk}/\bar{T} displayed in the upper panel and $\bar{T} = 5.5$.

V. POWER SPECTRUM

To show that T_{kk} also encodes the dynamics of fluctuations, we compute the power spectrum $S(\omega)$ of the chain length $R_N - R_0 + N l_0$ in the frequency domain, a quantity typically monitored in experiments [8]. According to the Wiener-Khinchin theorem [23], under stationary conditions $S(\omega)$ is given by the Fourier transform of the chain length's autocorrelation function. Referring again to free boundary conditions, in terms of normal modes we have $R_N - R_0 = \sum_{k=1}^N (\Phi_{Nk} - \Phi_{0k}) X_k$. Hence (Appendix D)

$$S(\omega) = \frac{2\gamma}{N+1} \sum_{k,k'=1}^N \frac{(\Phi_{Nk} - \Phi_{0k})(\Phi_{Nk'} - \Phi_{0k'}) T_{kk'}}{(\omega_k^2 - \omega^2 - i\gamma\omega)(\omega_{k'}^2 - \omega^2 + i\gamma\omega)} \quad (13)$$

$$\simeq \frac{16\gamma}{N+1} \sum_{\text{odd } k} \frac{\cos^2\left(\frac{k}{2(N+1)}\pi\right) T_{kk}}{(\omega_k^2 - \omega^2)^2 + \gamma^2\omega^2} \quad (14)$$

($\omega \neq 0$), where even modes do not contribute owing to the symmetry of the boundaries. Equation (14) neglects the cross correlations between modes at different k . Such cross-correlation terms are instead responsible for the heat flux along the chain, $J_n = l_0\kappa \langle \dot{R}_n R_{n-1} \rangle$ [12]. In terms of normal modes we have (Appendix D) in fact

$$J_n = -\frac{i l_0 \kappa}{(2\pi)^2} \frac{2\gamma}{N+1} \sum_{k \neq k'} \Phi_{nk} \Phi_{n-1,k'} T_{kk'} \times \int d\omega \frac{\omega}{(\omega_k^2 - \omega^2 - i\gamma\omega)(\omega_{k'}^2 - \omega^2 + i\gamma\omega)} \quad (15)$$

($0 < n < N$). We have checked that the contribution of terms with $k' \neq k$ in Eq. (13) can only be appreciated in proximity

of the negative peaks of the power spectrum, away from the resonances ω_k .

VI. CONCLUSIONS

In summary, our analytic study of energy repartition in a harmonic chain in contact with independent heat baths shows that both long and short wavelength modes may have energies which deviate significantly from the level expected if equipartition were to hold. This enhanced or reduced storage of energy depends critically on the shape of the temperature profile and on the boundary conditions. Other dynamical properties, such as the damping or the elastic coupling, are instead totally irrelevant. Thus, for a generic harmonic chain, information encoded in the temperature profile is mapped into a sequence of vibrational mode temperatures, which in turn shape the power spectrum of the chain length. Investigations about the influence on the above picture of nonlinearities originating thermomechanical couplings is the next important step.

ACKNOWLEDGMENTS

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APPENDIX A: BOUNDARY CONDITIONS

1. Free boundary conditions

In the case of free boundary conditions with $N+1$ oscillators the Laplacian matrix is

$$A \equiv (A_{nm})_{n,m=0,1,\dots,N} \equiv \begin{pmatrix} +1 & -1 & 0 & \cdots & 0 \\ -1 & +2 & -1 & \ddots & \vdots \\ 0 & -1 & \ddots & \ddots & \\ \vdots & \ddots & \ddots & & -1 & 0 \\ 0 & \cdots & & & -1 & +2 & -1 \\ & & & & 0 & -1 & +1 \end{pmatrix}, \quad (A1)$$

which is diagonalized by the linear transformation $\Phi^{-1} A \Phi$, with

$$\Phi_{nk} = \begin{cases} 1, & k=0, \\ \sqrt{2} \cos\left(\frac{(2n+1)k}{2(N+1)}\pi\right), & k \neq 0, \end{cases} \quad (A2)$$

$$\Phi^{-1} = \frac{\Phi^t}{N+1}. \quad (A3)$$

It is straightforward to see that the definition

$$T_{kk} \equiv (N+1) \sum_{n=0}^N \Phi_{kn}^{-1} \Phi_{kn}^{-1} T_n \quad (A4)$$

leads to

$$\mathcal{T}_{kk} = \bar{T} \left[1 + \frac{\sum_{n=0}^N T_n \cos\left(\frac{2n+1}{N+1}k\pi\right)}{\sum_{m=0}^N T_m} \right] \quad (0 < k \leq N) \quad (\text{A5})$$

and $\mathcal{T}_{00} = \bar{T} \equiv \sum_{n=0}^N T_n / (N+1)$. Notice that $\sum_{n=0}^N \cos\left(\frac{2n+1}{N+1}k\pi\right) = 0$, so that at equilibrium, $T_n = \bar{T} \forall n$, we recover $\mathcal{T}_{kk} = \bar{T} \forall k$.

2. Fixed boundary conditions

In the case of fixed boundary we can stick to our notations by fixing the two masses at the border. The number of oscillators becomes $N-1$, and the Laplacian matrix reads

$$A \equiv (A_{nm})_{n,m=0,1,\dots,N-1} \equiv \begin{pmatrix} 0 & 0 & 0 & \dots & 0 \\ 0 & +2 & -1 & \ddots & \vdots \\ 0 & -1 & \ddots & \ddots & \\ \vdots & \ddots & \ddots & & -1 & 0 \\ 0 & \dots & & -1 & +2 & 0 \\ 0 & \dots & & 0 & 0 & 0 \end{pmatrix}, \quad (\text{A6})$$

which now is diagonalized by

$$\Phi_{nk} = \begin{cases} \sqrt{N}, & (n,k) = (0,0) \text{ or } (n,k) = (N,N), \\ 0, & (0 < n \leq N, k = 0) \text{ or } (0 < n \leq N, k = N), \\ \sqrt{2} \sin\left(\frac{nk}{N}\pi\right), & \text{otherwise,} \end{cases} \quad (\text{A7})$$

$$\Phi^{-1} = \frac{\Phi^t}{N}. \quad (\text{A8})$$

Also in this case it is straightforward to show that

$$\mathcal{T}_{kk} = \frac{(N-1)\bar{T}}{N} \left[1 - \frac{\sum_{n=1}^{N-1} T_n \cos\left(\frac{2nk}{N}\pi\right)}{\sum_{m=1}^{N-1} T_m} \right] \quad (0 < k < N), \quad (\text{A9})$$

with $\bar{T} \equiv \sum_{n=1}^{N-1} T_n / (N-1)$. We have $\sum_{n=1}^{N-1} \cos\left(\frac{2nk}{N}\pi\right) = -1$, so that at equilibrium we again recover $\mathcal{T}_{kk} = \bar{T} \forall k$.

3. Mixed boundary conditions

In the case of mixed boundary we fix only the mass at $n=N$. The number of oscillators becomes N and the Laplacian matrix is

$$A \equiv (A_{nm})_{n,m=0,1,\dots,N} \equiv \begin{pmatrix} +1 & -1 & 0 & \dots & 0 \\ -1 & +2 & -1 & \ddots & \vdots \\ 0 & -1 & \ddots & \ddots & \\ \vdots & \ddots & \ddots & & -1 & 0 \\ 0 & \dots & & -1 & +2 & 0 \\ 0 & \dots & & 0 & 0 & 0 \end{pmatrix}, \quad (\text{A10})$$

which is diagonalized by the linear transformation $\Phi^{-1}A\Phi$ with

$$\Phi_{nk} = \begin{cases} \sqrt{\frac{2N+1}{2}} & (n,k) = (N,N), \\ 0 & (n=N, 0 \leq k < N) \text{ or } (0 \leq n < N, k=N), \\ \sqrt{2} \cos\left(\frac{(2n+1)(2k+1)}{2(2N+1)}\pi\right) & \text{otherwise,} \end{cases} \quad (\text{A11})$$

$$\Phi^{-1} = \frac{2\Phi^t}{2N+1}. \quad (\text{A12})$$

As for the previous cases, it is easy to prove that

$$\mathcal{T}_{kk} = \frac{2N\bar{T}}{2N+1} \left[1 + \frac{\sum_{n=0}^{N-1} T_n \cos\left(\frac{(2n+1)(2k+1)}{2N+1}\pi\right)}{\sum_{m=0}^{N-1} T_m} \right] \quad (0 \leq k < N), \quad (\text{A13})$$

with $\bar{T} \equiv \sum_{n=0}^{N-1} T_n / N$. In this case $\sum_{n=0}^{N-1} \cos\left(\frac{(2n+1)(2k+1)}{2N+1}\pi\right) = 1/2$, and again one recovers $\mathcal{T}_{kk} = \bar{T} \forall k$ at equilibrium.

APPENDIX B: ENERGY REPARTITION AMONG THE MODES

Equation

$$\ddot{X}_k = -\gamma \dot{X}_k - \omega_k^2 X_k + F_k \quad (\text{B1})$$

is a first-order linear differential equation in the vector $\mathbf{Y}_k \equiv (X_k, \dot{X}_k)$. Its stationary solution is formally given by

$$\mathbf{Y}_k(t) = \int_{-\infty}^t dt' \exp[(t-t')\Lambda_k] \cdot \mathbf{F}_k(t'), \quad (\text{B2})$$

with the definitions

$$\Lambda_k = \begin{pmatrix} 0 & 1 \\ -\omega_k^2 & -\gamma \end{pmatrix}, \quad \mathbf{F}_k = \begin{pmatrix} 0 \\ F_k \end{pmatrix}. \quad (\text{B3})$$

The matrix exponential in Eq. (B2) is computed by diagonalizing Λ_k . Its eigenvalues λ_k^{α} are the two solutions of the characteristic equation for the unforced harmonic oscillator, namely

$$\lambda_k^{\alpha} = \frac{1}{2}(-\gamma + (-1)^{\alpha-1} \sqrt{\gamma^2 - 4\omega_k^2}), \quad \alpha = 1, 2. \quad (\text{B4})$$

Therefore, from the solutions

$$X_k(t) = \sum_{\alpha=1,2} \int_{-\infty}^t dt' A_k^{\alpha} \exp(-\lambda_k^{\alpha}(t-t')) F_k(t'), \quad (\text{B5})$$

$$\dot{X}_k(t) = \sum_{\alpha=1,2} \int_{-\infty}^t dt' B_k^{\alpha} \exp(-\lambda_k^{\alpha}(t-t')) F_k(t'), \quad (\text{B6})$$

with

$$A_k^1 = \frac{1}{\lambda_k^2 - \lambda_k^1} = -A_k^2, \quad (\text{B7})$$

$$B_k^1 = -\frac{\lambda_k^1}{\lambda_k^2} B_k^2 = \lambda_k^1 A_k^2, \quad (\text{B8})$$

we can evaluate the stationary equal-time correlations

$$\langle X_k X_{k'} \rangle = 2\zeta \mathcal{T}_{kk'} \sum_{\alpha, \beta=1,2} \frac{A_k^\alpha A_{k'}^\beta}{\lambda_k^\alpha + \lambda_{k'}^\beta}, \quad (\text{B9})$$

$$\langle \dot{X}_k \dot{X}_{k'} \rangle = 2\zeta \mathcal{T}_{kk'} \sum_{\alpha, \beta=1,2} \frac{B_k^\alpha B_{k'}^\beta}{\lambda_k^\alpha + \lambda_{k'}^\beta}. \quad (\text{B10})$$

For the average kinetic and potential energy per mode,

$$K_k \equiv (N+1) \langle \dot{X}_k^2 \rangle (1 - \delta_{k0}/2), \quad (\text{B11})$$

$$V_k \equiv (N+1) \omega_k^2 \langle X_k^2 \rangle, \quad (\text{B12})$$

we thus obtain the basic result

$$K_k^X = V_k^X = \mathcal{T}_{kk}/2 \quad (k \neq 0). \quad (\text{B13})$$

APPENDIX C: RECONSTRUCTING THE TEMPERATURE PROFILE

Expressing the cosine in complex notation it is easy to prove the following identities:

$$\begin{aligned} \sum_{k=1}^N \cos\left(\frac{(2m+1)k}{N+1}\pi\right) \cos\left(\frac{(2n+1)k}{N+1}\pi\right) \\ = \frac{N+1}{2} \left(\delta_{mn} + \delta_{mN-n} \right) - 1, \end{aligned} \quad (\text{C1})$$

$$\sum_{k=1}^N \cos\left(\frac{(2m+1)k}{N+1}\pi\right) = 0. \quad (\text{C2})$$

Hence, from Eq. (6), we obtain

$$\sum_{k=1}^N \cos\left(\frac{(2m+1)k}{N+1}\pi\right) \mathcal{T}_{kk} \quad (\text{C3})$$

$$\begin{aligned} = \sum_{k=1}^N \cos\left(\frac{(2m+1)k}{N+1}\pi\right) \bar{T} \\ \times \left[1 + \frac{\sum_{n=0}^N T_n \cos\left(\frac{2n+1}{N+1}k\pi\right)}{\sum_{m=0}^N T_m} \right], \end{aligned} \quad (\text{C4})$$

or

$$T_n + T_{N-n} = 2 \sum_{k=1}^N \cos\left(\frac{2n+1}{N+1}k\pi\right) \mathcal{T}_{kk} + 2\bar{T}. \quad (\text{C5})$$

$$\langle \dot{X}_k X_{k'} \rangle = \frac{1}{(2\pi)^2} \int d\omega \int d\omega' (-i\omega) e^{-i\omega t} e^{i\omega' t} \langle \widehat{X}_k(\omega) \widehat{X}_{k'}^*(\omega') \rangle \quad (\text{D9})$$

$$= \frac{1}{(2\pi)^2} \int d\omega \int d\omega' (-i\omega) e^{-i\omega t} e^{i\omega' t} \frac{2\gamma}{N+1} \frac{\mathcal{T}_{kk'}}{(\omega_k^2 - \omega^2 - i\gamma\omega)(\omega_{k'}^2 - \omega'^2 + i\gamma\omega')} \delta(\omega - \omega') \quad (\text{D10})$$

$$= -\frac{i}{(2\pi)^2} \frac{2\gamma \mathcal{T}_{kk'}}{N+1} \int d\omega \frac{\omega}{(\omega_k^2 - \omega^2 - i\gamma\omega)(\omega_{k'}^2 - \omega^2 + i\gamma\omega)}. \quad (\text{D11})$$

Putting things together we obtain

$$J_n = -\frac{i l_0 \kappa}{(2\pi)^2} \frac{2\gamma}{N+1} \sum_{k \neq k'} \Phi_{nk} \Phi_{n-1, k'} \mathcal{T}_{kk'} \int d\omega \frac{\omega}{(\omega_k^2 - \omega^2 - i\gamma\omega)(\omega_{k'}^2 - \omega^2 + i\gamma\omega)} \quad (0 < n < N). \quad (\text{D12})$$

APPENDIX D: SPECTRAL DENSITY

According to the Wiener-Khinchin theorem [23], under stationary conditions the spectral density $S(\omega)$ of the chain length $R_N - R_0 + Nl_0$ is given by

$$\begin{aligned} S(\omega) = \int d\tau e^{i\omega\tau} \langle [R_N(t_0) - R_0(t_0)] \\ \times [R_N(t_0 + \tau) - R_0(t_0 + \tau)] \rangle + 2\pi N^2 l_0^2 \delta(\omega). \end{aligned} \quad (\text{D1})$$

We have

$$R_N(t) - R_0(t) = \sum_{k=1}^N (\Phi_{Nk} - \Phi_{0k}) X_k(t), \quad (\text{D2})$$

so that

$$\begin{aligned} S(\omega) = \sum_{k, k'=1}^N (\Phi_{Nk} - \Phi_{0k})(\Phi_{Nk'} - \Phi_{0k'}) \\ \times \int d\tau e^{i\omega\tau} \langle X_k(t_0) X_{k'}(t_0 + \tau) \rangle + 2\pi N^2 l_0^2 \delta(\omega). \end{aligned} \quad (\text{D3})$$

We indicate the Fourier transform of a generic function $h(t)$ as $\widehat{h}(\omega) \equiv \int dt e^{i\omega t} h(t)$, and denote its complex conjugate as $\widehat{h}^*(\omega)$. The Fourier transform of Eq. (4) gives

$$-\omega^2 \widehat{X}_k(\omega) = i\omega\gamma \widehat{X}_k(\omega) - \omega_k^2 \widehat{X}_k(\omega) + \widehat{\eta}_k(\omega). \quad (\text{D4})$$

Solving for $\widehat{X}_k(\omega)$ and using

$$\langle \eta_k(t) \eta_{k'}(t') \rangle = 2\gamma \mathcal{T}_{kk'} \delta(t - t') / (N+1) \quad (\text{D5})$$

we obtain, for $\omega \neq 0$,

$$S(\omega) = \frac{2\gamma}{N+1} \sum_{k, k'=1}^N \frac{(\Phi_{Nk} - \Phi_{0k})(\Phi_{Nk'} - \Phi_{0k'}) \mathcal{T}_{kk'}}{(\omega_k^2 - \omega^2 - i\gamma\omega)(\omega_{k'}^2 - \omega^2 + i\gamma\omega)}. \quad (\text{D6})$$

The local heat flux J_n along the chain [12] is given by

$$J_n = l_0 \kappa \langle \dot{R}_n R_{n-1} \rangle \quad (0 < n < N). \quad (\text{D7})$$

In terms of normal modes the local heat flux becomes

$$J_n = l_0 \kappa \sum_{k \neq k'} \Phi_{nk} \Phi_{n-1, k'} \langle \dot{X}_k X_{k'} \rangle. \quad (\text{D8})$$

Indeed, stationarity implies $\langle \dot{X}_k X_k \rangle = 0$ for equal-time averages. We then have

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Chapter 4

Nonequilibrium linear response theory

In the previous chapter we have investigated some steady-state properties—the energetic and mechanical state—of various nonequilibrium Markov systems, comprising nonisothermal, driven and active matter. Here we move on to explore their dynamical (non-stationary) features caused by the small interaction with an external agent. Whether it is the probing manipulation of an experimenter or the weak coupling with an environment, the interaction is thought of as a small perturbation around a nonequilibrium state¹. Hence, what we are going to address is the linear response of driven Markov systems.

The goal of response theory is to figure out how a system’s observable \mathcal{O} reacts on average to outside influences. The basic assumption is that a perturbed average $\langle \mathcal{O} \rangle_\theta$ can be expanded in a functional Taylor series in the time-dependent perturbation θ . In the linear response regime, the perturbation is assumed small enough to truncate the series at the first order. One then aims at expressing the linear response function R_θ and the corresponding susceptibility χ_θ ,

$$R_{\mathcal{O},\theta}(t,t') \equiv \left. \frac{\delta \langle \mathcal{O}(t) \rangle_\theta}{\delta \theta(t')} \right|_{\theta=0}, \quad \chi_{\mathcal{O},\theta}(t) \equiv \int dt' R_{\mathcal{O},\theta}(t,t'), \quad (4.1)$$

in terms of *unperturbed* correlation functions $\langle \mathcal{O}(t) \dots \rangle$. These functions give the system’s response at time t to a kick at a previous time t' and to a constant perturbation, respectively. The unperturbed state, besides having to be stable, is arbitrary. When it coincides with equilibrium, linear response is a fully developed theory whose trademark is the FDT—response and spontaneous fluctuations follow the same dynamics [9]. Conversely, for perturbations of nonequilibrium states, the theory is far more fragmented and still incomplete [52, 108–122].

The main obstacle to surmount is the fact that nonequilibrium probability distributions are in general unknown. This poses technical problems not present in equilibrium. There, one expands in the perturbing field the Gibbs distribution, or the propagator acting on an initial Gibbs state, to obtain the static susceptibility $\chi_{\mathcal{O},\theta}(\infty)$ and dynamic response R_θ , respectively. Out of equilibrium, the absence of a known unperturbed distribution² to operate on makes the first procedure simply inapplicable. The second,

¹Such unperturbed state may be non-stationary as well, like in aging glasses.

²Actually, for deterministic thermostatted systems (see Chapter 5) probability densities are even singular objects. It is due to the dissipative forces that induce a phase space contraction, and thus a concentration of probabilities into attractors of zero measure [123]. A rigorous treatment cannot be based on probability densities [124].

instead, reduces to a formal expansion with, in general, no clear physical interpretation nor practical implementability³.

These difficulties can be overcome by a slight change of approach, in which the attention is shifted from phase space probabilities to probabilities defined on the functional space of trajectories [119, 120]. Namely, one assigns a weight $P_\theta[\mathbf{x}] \propto \exp \mathcal{A}_\theta[\mathbf{x}]$ to any time-ordered set of states $[\mathbf{x}]$ that the perturbed dynamics traverse. Knowledge of the (stochastic) dynamical equations is thus sufficient to construct the action $\mathcal{A}_\theta[\mathbf{x}]$, which is in turn amenable to a systematic expansion in the small perturbation amplitude θ .

Let us focus first on mechanical perturbations consisting in, e.g., an additional external potential energy $V(\mathbf{x})$ modulated in time by θ . The linear response (4.1) evaluated through the path integral

$$R_{\mathcal{O},\theta}(t,t') = \int D\mathbf{x} \mathcal{O}(t) \frac{\delta e^{\mathcal{A}_\theta[\mathbf{x}]}}{\delta \theta(t')} \Big|_{\theta=0} = \frac{1}{2} \langle \mathcal{O}(t) \dot{S}(t') \rangle - \langle \mathcal{O}(t) \dot{K}(t') \rangle, \quad (4.2)$$

is naturally expressed by splitting the action derivative $\delta \mathcal{A}_\theta / \delta \theta|_{\theta=0}$ in the antisymmetric ($\dot{S}/2$) and symmetric ($-\dot{K}$) part with respect to time reversal. Equation (4.2) is a ready-made expression giving the response in terms of correlation functions measured in the unperturbed, nonequilibrium state. Imposing the condition of local detailed balance is then sufficient to assign a thermodynamic meaning to the antisymmetric function \dot{S} . It keeps the form of a heat rate, $\partial_{\mathbf{x}} V \cdot \dot{\mathbf{x}} = \dot{V}$, divided by the system's bath temperature T , for it represents the entropy flow into the bath caused by the perturbation⁴. The time-symmetric quantity $K(t')$ has instead a purely dynamical significance, namely, it is proportional to the $O(h)$ variation in the escape rate (from the state $\mathbf{x}(t')$) due to the perturbation. Since it measures how frantic the dynamic is, it is often named dynamical activity [119, 126–130]. In equilibrium its role is not manifest, as it gives a contribution equal to the entropic term [119], yielding the celebrated Kubo formula⁵ ($k_B = 1$),

$$R_{\mathcal{O},\theta}^{\text{Kubo}}(t,t') = \langle \mathcal{O}(t) \dot{S}(t') \rangle = \frac{1}{T} \frac{d}{dt'} \langle \mathcal{O}(t) V(t') \rangle. \quad (4.3)$$

Thanks to the canonical structure of the Gibbs statistics, the equilibrium response is seen to involve the observable (V) conjugated with the perturbation (θ) via the Boltzmann factor. Local detailed balance lifts up this canonical structure to dynamics [131] so that the observables involved in (4.2) are those conjugated to the perturbation through the action \mathcal{A} .

Mechanical forces do not exhaust the range of possible perturbations a system may undergo. Equally important are the perturbations in the thermodynamic parameters (temperature, pressure, chemical potential) of the system's reservoirs. The associated long-time responses correspond to thermodynamic susceptibilities (e.g. heat capacity, thermal expansivity, compressibility), which are central quantities needed in the construction of an extended thermodynamics of steady states [92, 93]. In equilibrium, thermodynamic functions enter directly the system's Gibbs distribution, paired by their respective conjugated variables. Hence, such canonical structure yields again the long-time susceptibilities. For example, taking the system energy as the observable

³For the simple systems considered in [53, 55] we could follow this route, additionally. This should be considered as an exception rather than the rule, though.

⁴The identification holds even in non-Markovian systems [125].

⁵Causality implies the response to vanish for $t' > t$.

$\mathcal{O} = U$, and the temperature perturbation θT , whose conjugated quantity is U/T , we immediately retrieve the equilibrium heat capacity

$$C = \lim_{t \rightarrow \infty} \chi_{U,T}^{\text{Kubo}}(t) = \frac{1}{T^2} \langle U^2 \rangle. \quad (4.4)$$

Contrarily, out of equilibrium the action of effective (heat, pressure, particle) reservoirs has to be included in the system's dynamical equations and the result of their perturbation has to be worked out explicitly.

As far as stochastic systems are considered, the Langevin formalism is arguably the best playground to implement thermal perturbations, thanks to its broad applicability [132–136]. There, varying the temperature (of one or more baths) corresponds to changing the amplitude of Gaussian noises. Such an apparently armless operation is in fact potentially disastrous when the approach based on trajectory probabilities is considered. Path weights corresponding to different temperatures are indeed incommensurable, so that (a naive) linear response theory turns out to be plagued by divergences [134, 137]. Clearly, one would like to obtain finite results without recurring to explicit discretizations in order to unravel the physics underlying the thermal response.

In our work, based on two distinct techniques, we undertake this task. In [53] we bypass the problem *in toto* by means of an intuitive rescaling of the Langevin coordinates that transforms thermal forces into mechanical ones. In [49] we proceed with an explicit regularization of the divergences via a novel functional method. These two independent methods yield a physical picture of thermal response very analogous to that of mechanical response. Namely, entropic contributions and non-dissipative aspects turn out to be equally relevant, differently from equilibrium where perturbed states relax back to a new steady regime solely by dissipation. This may suggest that the structure of (4.2) carries over not only to thermal variations but also to other thermodynamic perturbations. Being the dynamical aspects encoded in K peculiar to any system and different for different perturbations, one has to renounce the formal simplicity of equilibrium results. Nonetheless, the general approach based on path probabilities accomplishes the goal of giving responses in terms of unperturbed correlation functions, which means in practice, predicting and experimentally inferring the system response without actually disturbing it.

In order to show the validity of our results we have considered two different experimental setups, namely, an RC-circuit [54] and two trapped colloidal particles interacting hydrodynamically [55]. In both cases the various system components are maintained at two different controllable temperatures, and the susceptibility of the internal energy is inferred from stationary measurements. The correctness of the long time limit, giving the nonequilibrium heat capacity of the systems, is checked against the theoretical prediction of the mesoscopic virial equation. The transient response is favorably compared with an equivalent response formula based on expanding the nonequilibrium phase space distribution, which is exactly computable in this case thanks to the relative simplicity of the dynamics.

Finally, let us note that the external perturbation is not necessarily a deliberate operation made by an experimenter to probe some system property. It may as well result from a small coupling with an additional (uncontrolled) system possessing its own dynamics. As such, response theory can be used to coarse-grain weakly interacting systems, by averaging over nonequilibrium degrees of freedom. We implement this procedure in [56], where we consider a system \mathbf{Q} interacting with a driven environment \mathbf{x} , whose motion is not under direct control. The fluctuations of \mathbf{Q} around a preferred

state influence \boldsymbol{x} , which in turns feeds back energy to Q . If the two systems are weakly coupled, such reaction can be calculated as the linear response of \boldsymbol{x} to small variations in the external parameter Q [138]. The \boldsymbol{x} dynamics is thus eliminated from the Q equations of motion and subsumed into dissipative and noisy forces breaking the fluctuation-dissipation theorem, and effective interactions not satisfying the action-reaction law. Ideally, the reduced equation of motion enables one to infer the key properties of the nonequilibrium environment from the observed mesoscopic dynamics.

Temperature response in nonequilibrium stochastic systems

GIANMARIA FALASCO¹ and MARCO BAIESI^{2,3}

¹ *Institut für Theoretische Physik, Universität Leipzig - Postfach 100 920, D-04009 Leipzig, Germany*

² *Department of Physics and Astronomy, University of Padova - Via Marzolo 8, I-35131 Padova, Italy*

³ *INFN - Sezione di Padova - Via Marzolo 8, I-35131 Padova, Italy*

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Abstract – The linear response to temperature changes is derived for systems with overdamped stochastic dynamics. Holding both in transient and steady-state conditions, the results allow to compute nonequilibrium thermal susceptibilities from unperturbed correlation functions. These correlations contain a novel form of entropy flow due to temperature unbalances, next to the standard entropy flow of stochastic energetics and to complementary time-symmetric dynamical aspects. Our derivation hinges on a time rescaling, which is a key procedure for comparing apparently incommensurable path weights. An interesting notion of thermal time emerges from this approach.

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In thermodynamic equilibrium, the linear response coefficients for perturbing forces (*e.g.*, conductivity as a response to an electric potential) and perturbed temperatures (*e.g.*, thermal expansion coefficients or specific heats) may be computed with the fluctuation-dissipation theorem. So-called Kubo formulas relate the response to the unperturbed correlation between the observable and the entropy produced by the perturbation [1]. Out of equilibrium such a clear picture is lacking yet.

For nonequilibrium systems the standard linear response to deterministic forcing has been developed via many approaches (see, *e.g.*, [2–14]). In comparison, there is a small number of results obtained for the response to temperature changes [15–20]. For example there is no formula to express, as a function of steady-state unperturbed correlations, the thermal expansion coefficient for a solid kept in a temperature gradient (*e.g.*, as in experimental setups [21,22] or in models of coupled oscillators [23,24]). The construction of a general steady-state thermodynamics [25–32] needs at its heart the understanding of temperature responses, for example in defining nonequilibrium specific heats [16]. A nonequilibrium thermal response should as well be the subject of study in related fields, such as climatology [33–35].

This paper introduces a theory for the linear response to a change of the reservoirs' temperature, valid also in transient conditions. We consider nonequilibrium overdamped systems. Mesoscopic systems of this

kind, including driven colloids [36,37] and active matter [38], are used as paradigms in the attempt to generalize equilibrium concepts, such as free energies, within the framework of a steady-state thermodynamics [25–32]. Moreover, they offer the possibility to observe experimentally the statistical fluctuations of energy fluxes [39,40].

Our approach is inspired by a scheme based on path weights and developed for the response to forces [13,14]. For that theory the response turns out to be the sum of two terms, as in previous studies [3,11,12]. The first one is half of the unperturbed correlation $\langle OS \rangle$ between the observable \mathcal{O} and entropy S produced by the perturbation, *i.e.* half of a Kubo formula. The second is the correlation $-\langle OK/2 \rangle$, where the term $-K/2$, of which we still have a less intuitive grasp, is the time-symmetric part of the action weighting the system's trajectories. In order to avoid singularities emerging in a related temperature response [17] based on a time-discretization, we introduce a time rescaling that significantly changes the derivation. As a result, the susceptibility is written as a sum of unperturbed correlations containing well-defined (stochastic) integrals. Moreover, an intriguing and unexpected picture emerges: in S , the heat fluxes as described in the context of stochastic energetics [25,41,42] appear accompanied by a second form of entropy production (not present in [17]), which is relevant when the system is coupled to reservoirs at different temperatures.

The overdamped diffusive system we consider is described by $i = 1, \dots, N$ degrees of freedom $x = \{x_i\}$, evolving in the unperturbed state as

$$\dot{x}_i(t) = F_i(x(t)) + \sqrt{T_i(t)} \xi_i(t), \quad (1)$$

where every Gaussian white noise ξ_i is uncorrelated with the others, $\langle \xi_i(t) \xi_j(t') \rangle = 2\delta_{ij} \delta(t - t')$. For $t > 0$, the constant bath temperatures T_i 's are modulated by the time-dependent parameter $h(t) \ll 1$, so that (1) becomes

$$\dot{x}_i(t) = F_i(x(t)) + \sqrt{\Theta_i(t)} \xi_i(t), \quad (2)$$

where $\Theta_i(t) = T_i[1 + \epsilon_i h(t)]$ stands for the perturbed temperature of reservoir i . For simplicity, in particular, we choose a subset \mathcal{T} so that $T_i = T$ if $i \in \mathcal{T}$, which is then considered as a single heat bath to be perturbed. An indicator function, $\epsilon_i = 1$ only if $i \in \mathcal{T}$ and $\epsilon_i = 0$ otherwise, is useful to keep track of the perturbed degrees of freedom¹. We seek the linear response of a generic state observable $\mathcal{O}(x)$ to the described change in T , namely,

$$R_{\mathcal{O}T}(t, t') \equiv \left. \frac{1}{T} \frac{\delta \langle \mathcal{O}(t) \rangle^h}{\delta h(t')} \right|_{h=0}. \quad (3)$$

Note that temperatures do not depend on the coordinates, hence there is no ambiguity in the interpretation of the stochastic equation. Throughout this paper we will always consider the Stratonovich convention (hence, the midpoint rule is used for discretizing (1) and (2)), implying standard rules of functional calculus [43]. The system may be brought far from equilibrium a) by generic nonconservative forces F_i , b) by different T_i 's, and c) by a relaxation from an initial transient condition. Indeed, given that the perturbation is turned on at times $t > 0$, the initial density of states $\rho_0(x)$ at $t = 0$ may coincide or not with a steady-state density. For economy of notation we do not recall this explicitly in the statistical averages, denoted by $\langle \dots \rangle^h$ and $\langle \dots \rangle$ for the perturbed ($h \neq 0$) and unperturbed ($h = 0$) case, respectively.

The backward generator associated to the Markovian dynamics (1) is

$$\mathbb{L} = \sum_{j=1}^N \mathbb{L}_j \quad \text{with} \quad \mathbb{L}_j = F_j(x) \partial_{x_j} + T_j \partial_{x_j}^2, \quad (4)$$

written in a notation that will be useful later. Next to this standard operator we define a new modified generator that is useful to describe the temperature response, when the temperature T of a reservoir is altered:

$$\mathbb{L}^{(T)} \equiv \sum_{j=1}^N \frac{T}{T_j} \mathbb{L}_j = \sum_{j=1}^N \left(\frac{T}{T_j} F_j(x) \partial_{x_j} + T \partial_{x_j}^2 \right), \quad (5)$$

which acts on the observables as if all temperatures were equal to T and all forces F_j were rescaled by T/T_j . While

¹Note that more general conditions on ϵ and T may be imposed with the same formalism.

\mathbb{L} gives the derivative of a state observable \mathcal{O} with respect to the kinematic time t , *i.e.* $\langle \mathbb{L} \mathcal{O} \rangle = \partial_t \langle \mathcal{O} \rangle$, $\mathbb{L}^{(T)}$ gives the variation of each degree of freedom with respect to its own *thermal* time $\tau_j \equiv tT_j/T$, namely,

$$\langle \mathbb{L}^{(T)} \mathcal{O} \rangle = \left\langle \sum_j \frac{dx_j}{d\tau_j} \partial_{x_j} \mathcal{O} \right\rangle \equiv \frac{d}{dt}^{(T)} \langle \mathcal{O} \rangle, \quad (6)$$

such that a generalized time derivative results defined.

Before spelling out the derivation of our results, some physical insights on the meaning of a temperature change can be gained by performing the time transformation $Td\tau = \Theta(t)dt$ in eq. (2) (here, with a slight abuse of notation, we are using the same symbol τ both for the perturbed and unperturbed thermal time). Taking $N = 1$ for simplicity, upon perturbation (1) becomes to first order in h

$$\dot{x}(\tau) \simeq [1 - h(\tau)]F(x(\tau)) + \sqrt{T} \xi(\tau), \quad (7)$$

which clearly shows that, in such time coordinate, a temperature perturbation is equivalent to a force perturbation. The response to a small decrease in F is given by a theory of nonequilibrium linear response [14] as

$$R_{\mathcal{O}F}(\tau, \tau') = -\frac{1}{2T} \left\langle \mathcal{O}(\tau) [\dot{x}(\tau')F(\tau') - \dot{K}(\tau')] \right\rangle, \quad (8)$$

where $\dot{K}(x(\tau')) = F^2(x(\tau')) + T\partial_x F(x(\tau'))$. If the system were in equilibrium, so that $F = -\partial_x \mathcal{H}$ with \mathcal{H} the system's Hamiltonian, one would expect the correlation functions to be invariant under a time reparametrization. Therefore, from (8) the response to a temperature change in equilibrium is obtained as

$$R_{\mathcal{O}T}(t - t') = \frac{1}{2T^2} \left\langle \mathcal{O}(t) [\dot{\mathcal{H}}(t') - \mathbb{L}\mathcal{H}(t')] \right\rangle,$$

which is recognized as a Kubo formula, since in equilibrium $\langle \mathcal{O}(t) \mathbb{L}\mathcal{H}(t') \rangle = -\langle \mathcal{O}(t) \dot{\mathcal{H}}(t') \rangle$ [13]. Out of equilibrium instead $R(\tau, \tau')$ depends implicitly on h through the time variables and no further simplification of (8) appears possible.

Nevertheless, the diffusive character of the system suggests to replace the above time change with the space coordinate change $y_i(t)/\sqrt{T_i} = x_i(t)/\sqrt{\Theta_i(t)}$ [44], so that (2) reads

$$\dot{y}_i(t) = \sqrt{\frac{T_i}{\Theta_i}} F_i(x(y)) - \frac{1}{2} y_i(t) \frac{\dot{\Theta}_i}{\Theta_i} + \sqrt{T_i} \xi_i. \quad (9)$$

Perturbed averages are now calculated with the path weights for the process y , *i.e.* the statistical weight $P^h[y]$ of the trajectory $\{y(s) : 0 \leq s \leq t\}$. In particular, for all times $0 < t' < t$ and any state observable \mathcal{O} , the linear response is evaluated as²

$$R_{\mathcal{O}T}(t, t') = \int \mathcal{D}y \mathcal{O}(y(t)) \left. \frac{\delta P^h[y]}{\delta h(t')} \right|_{h=0}. \quad (10)$$

²If \mathcal{O} is a functional of the trajectory, *i.e.* it is extensive in time like, *e.g.*, heat flows, the response contains the additional term $\langle \frac{\delta \mathcal{O}}{\delta h(t')} \rangle|_{h=0}$.

Here, only terms of order $O(h)$ are needed, hence we can directly linearize the Langevin equation (9) obtaining

$$\dot{y}_i \simeq F_i(y) + \frac{h}{2} f_i(y) - \frac{\epsilon_i}{2} \dot{h} y_i + \sqrt{T_i} \xi_i, \quad (11)$$

where we recognize a standard perturbing force,

$$f_i = \sum_{j=1}^N \epsilon_j y_j \partial_{y_j} F_i - \epsilon_i F_i, \quad (12)$$

and a second one, $-\dot{h}\epsilon_i y_i/2$, which is atypical in that it is modulated by $\dot{h}(t)$. Note that in expanding the force F_i it is implicitly required that the values of y_i are bounded.

The path weight $P^h[y]$ is obtained with a standard procedure from the Gaussian path weight for ξ , regarding ξ as a functional of y via (11) [45]:

$$P^h[y] \propto \prod_{i=1}^N \exp \left\{ -\frac{1}{4T_i} \int_0^t ds [\dot{y}_i - F_i - \frac{1}{2}(h f_i - \epsilon_i \dot{h} y_i)]^2 - \frac{1}{2} \int_0^t ds [\partial_{y_i} F_i + \frac{1}{2}(h \partial_{y_i} f_i - \epsilon_i \dot{h})] \right\} \quad (13)$$

(the dependence of all terms on the time s is understood). Plugging (13) in (10) we encounter the modulation \dot{h} , which wraps in a time derivative the standard result valid for deterministic perturbations, namely $\frac{\delta}{\delta h(t')} \int_0^t ds \dot{h} [y_i(\dot{y}_i - F_i)] = -\partial_{t'} [y_i(\dot{y}_i - F_i)]$. Next we assume $\partial_{y_j} F_i = \partial_{y_i} F_j$, which covers the most common physical conditions of irrotational forces and two-body potential interactions, leaving the more general case for a future work. By massaging the formulas and using $y_i|_{h=0} = x_i$ we finally derive

$$\left. \frac{\delta P^h[y]}{\delta h(t')} \right|_{h=0} = \sum_i \frac{\epsilon_i}{4} \left\{ -\frac{2F_i \dot{x}_i}{T_i} + \frac{F_i^2}{T_i} - x_i \sum_j \frac{\mathbb{L}_j F_i}{T_j} + x_i \sum_j \left(\frac{1}{T_j} - \frac{1}{T_i} \right) \dot{x}_j \partial_{x_j} F_i + \frac{1}{2T_i} \frac{d^2 x_i^2}{dt'^2} \right\} (t') P[x]. \quad (14)$$

Given our choice $\epsilon_i = 1$ for $i \in \mathcal{T}$, the response function of $\mathcal{O}(t)$ to the variation of T is thus written as

$$R_{\mathcal{O}T}(t, t') = \sum_{i \in \mathcal{T}} \frac{1}{4T^2} \left\{ -2\langle \mathcal{O}(t) F_i(t') \dot{x}_i(t') \rangle \right. \quad (15a)$$

$$\left. + \left\langle \mathcal{O}(t) \sum_{j \notin \mathcal{T}} \left(\frac{T}{T_j} - 1 \right) [x_i \dot{x}_j \partial_{x_j} F_i](t') \right\rangle \right. \quad (15b)$$

$$\left. + \langle \mathcal{O}(t) F_i^2(t') \rangle - \left\langle \mathcal{O}(t) x_i(t') \mathbb{L}^{(T)} F_i(t') \right\rangle \right. \quad (15c)$$

$$\left. + \frac{1}{2} \frac{d^2}{dt'^2} \langle \mathcal{O}(t) x_i^2(t') \rangle \right\}. \quad (15d)$$

In (15a) $J_i = -F_i \dot{x}_i$ is the heat flux from the i -th bath [41]. In addition, in (15b) there appears a novel

kind of heat flux,

$$\begin{aligned} J_i^{\text{int}}(t') &= x_i \sum_j \left(\frac{T}{T_j} - 1 \right) \dot{x}_j \partial_{x_j} F_i \\ &= \left(\frac{d}{dt'} \right)^{(T)} (x_i F_i) = - \sum_j \left(\frac{dx_j}{d\tau'} - \frac{dx_j}{dt'} \right) \partial_{x_j} V_i, \end{aligned} \quad (16)$$

which vanishes when kinematic and thermal times coincide, *i.e.* when the system is isothermal previous to the perturbation. The virial $V_i \equiv -x_i F_i$ of the i -th degree of freedom (whose average value equals $T_i = T$ even in a nonequilibrium steady state [46]) is seen to act as a potential energy for x_j . The meaning of J_i^{int} is thus understood as the difference between the heat absorption rate in the kinematic time and that in the thermal time, generated by forces $\partial_{x_j} V_i$ on x_j 's. One could also prove [47] the relation

$$\frac{1}{T} J_i^{\text{int}}(t') = -x_i(t') \frac{\delta \mathcal{S}}{\delta x_i(t')}, \quad (17)$$

which expresses the heat flux J_i^{int} in terms of the variation of the integrated entropy flux into the reservoirs, *i.e.* $\mathcal{S} \equiv \int_0^t ds \sum_{j=1}^N J_j(s)/T_j$, upon displacement of x_i . Thus, the total entropy flux from the selected heat bath to the system, $\sum_{i \in \mathcal{T}} J_i/T$, is side by side with the entropy flux $\sum_{i \in \mathcal{T}} J_i^{\text{int}}/T$ due to the heat currents installed within the system by the presence of different coupled temperature reservoirs. These two terms are time-antisymmetric, that is, they change sign by going through the trajectory backward in time. The remaining terms, namely (15c) and (15d) contain the correlation between the observable and time-symmetric quantities.

During the last decade there was an increase of interest in time-symmetric fluctuating quantities (see, *e.g.*, [13,48–52]), as it is becoming clearer that they must complement entropy fluxes for a deeper understanding of statistical mechanics. For example, the dynamical activity of a jump process (counting the number of jumps) is a key aspect for characterizing glassy dynamics [48,49,51,52]. In linear response it was found that the time-symmetric sector of path weights is often related to the mean tendency of the system to change the perturbing potential, *e.g.* for jump processes it becomes a shift in escape rates [13,14]. The adjective “frenetic” was used to label this property [13,14,53].

In (15c) we find frenetic contributions that do depend explicitly on forces of the system while the last term (15d) does not. The presence of such term is necessary for having a possibly non-zero response also for free diffusion. For example, for a free particle starting from $x(0) = 0$ the theory yields a response of the mean square displacement $\langle x^2(t) \rangle$ to an increase of T which is correctly $R_{x^2 T}(t, t') = \frac{1}{8T^2} \frac{d^2}{dt'^2} \langle x^2(t) x^2(t') \rangle = 2$ (or more in general twice the mobility, if we had put such constant in front of

the forces³; the calculation considers the Gaussian statistics and uses Wick's theorem).

Upon integration of (15) we get the susceptibility

$$\chi_{\mathcal{O}T}(t) \equiv \int_0^t dt' R_{\mathcal{O}T}(t, t') = \frac{1}{2T} [\langle \mathcal{O}(t)S \rangle - \langle \mathcal{O}(t)K \rangle], \quad (18)$$

where S , the entropy change of reservoir \mathcal{T} , contains the Stratonovich integrals of (15a) and (15b), while the ‘‘frenesy’’ K contains the remaining integrals of (15c) and (15d). In $-K$ in particular there appears a pair of boundary terms $\frac{1}{4T} \frac{d}{dt'} \langle \sum_{i \in \mathcal{T}} x_i^2(t') \mathcal{O}(t) \rangle \Big|_{t'=0}^{t'=t}$ in which left derivatives are performed to keep $t' \leq t$.

As an example, we show the susceptibility of the energy ($\mathcal{O} = \mathcal{H}$) to a change of T in a model of elastic slab between two thermostats. Due to the conservative nature of the internal forces, the total heat absorbed from the environment by the system, $\mathcal{Q}(t) = \sum_{i=1}^N \int_0^t dt' J_i(t')$, equals the change in internal energy. Hence

$$\frac{\delta}{\delta h(t')} \langle \mathcal{Q}(t) \rangle \Big|_{h=0} = \frac{\delta}{\delta h(t')} \langle \mathcal{H}(t) \rangle \Big|_{h=0} \quad (19)$$

and the susceptibility $\chi_{\mathcal{H}T}(t)$ associated to such response function is a form of nonequilibrium heat capacity.

The system is simulated using a Heun scheme [41] so that the points of the trajectory can be used in discretized Stratonovich integrals. A scalar x_i is defined for i labeling a site in a portion $L \times L \times 2$ of a cubic lattice. Each x_i in the lower $L \times L$ layer is thermalized at T while the x_i 's in the upper sites are maintained at $T_2 \neq T$, so that the system is out of equilibrium due to a constant heat flux. The total energy is $\mathcal{H} = \sum_i u(x_i) + \sum_{i \div j} u(x_i - x_j)$ with $u(x) = \frac{x^2}{2} + \frac{x^4}{4}$ ($i \div j$ indicates the nearest-neighbor pairs, with periodic boundary conditions within each layer). We compute $\chi_{\mathcal{H}T}(t)$ both by direct application of a constant perturbation $\Delta T = T \cdot 10^{-2}$ turned on at time $t = 0$,

$$\chi_{\mathcal{H}T}(t) = \frac{\langle \mathcal{H}(t) \rangle_{(T+\Delta T, T_2)} - \langle \mathcal{H}(t) \rangle_{(T, T_2)}}{\Delta T}, \quad (20)$$

and by (18). We find that the two estimates of the susceptibility are in good agreement. For instance, starting from the system in the steady state at $t = 0$, fig. 1(a) shows the results for a slab with $L = 5$, when $T = 2$, $T_2 = 3$. Since here a positive ΔT brings T closer to T_2 , in response the mean heat current $\langle J \rangle$ from the reservoir \mathcal{T} is lowered, as captured by the asymptotic anticorrelation between J and energy (integral of (15a) in fig. 1(a)). Hence, unlike in equilibrium, the entropy flux J/T is by itself not sufficient even for determining the global trend of the response. Figure 1 shows that all terms in (15) are relevant. To remind that the theory is applicable also

³Our results can be easily generalized if a mobility μ_i (the inverse of a damping constant) is associated with each degree of freedom: one just needs the replacements $F_i \rightarrow \mu_i F_i$ and $T_i \rightarrow \mu_i T_i$ in the formulas, besides for the $1/T$ prefactor in the definition of the response.

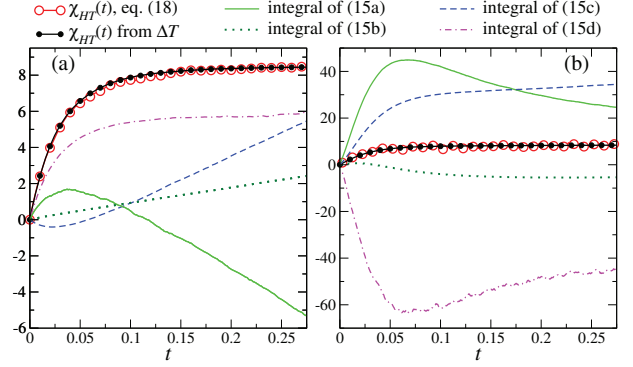


Fig. 1: (Color online) Susceptibility of the internal energy to a change of T in the elastic slab with fixed $T_2 \neq T$, computed both by the direct perturbation (20) and through (18): (a) steady state at $t = 0$, and (b) transient from a configuration given at $t = 0$. Terms of (18) specified in (15) are also shown.

to transient conditions, in fig. 1(b) we show results obtained by starting at $t = 0$ from a given configuration with $x_i = 1/2$ in the lower layer and $x_i = -1/2$ in the upper one. In a similar way, one might analyze data from a temperature quench as usually done for models of spins or glasses [3,11,12,49,51].

The response formula (15) simplifies when all the reservoirs are at the same temperature previous to the perturbation, because $J^{\text{int}} = 0$ and $\mathbb{L}^{(T)} = \mathbb{L}$:

$$R_{\mathcal{O}T}(t, t') = \sum_{i \in \mathcal{T}} \frac{1}{4T^2} \left\{ 2 \langle \mathcal{O}(t) J_i(t') \rangle + \frac{1}{2} \frac{d^2}{dt'^2} \langle \mathcal{O}(t) x_i^2(t') \rangle + \langle \mathcal{O}(t) F_i^2(t') \rangle - \langle \mathcal{O}(t) x_i(t') \mathbb{L} F_i(t') \rangle \right\}. \quad (21)$$

Moreover, if the system is in a nonequilibrium steady state, \mathbb{L} can be conveniently expressed in terms of the generator of the dynamics reversed in time, \mathbb{L}^* , as $\mathbb{L} = \mathbb{L}^* + 2v \cdot \nabla_x$, with $v = J/\rho$ the state velocity, *i.e.* the probability current over the probability density [6]. Taking for simplicity only one degree of freedom x , it is possible⁴ to recast the temperature response in the form

$$R_{\mathcal{O}T}(t - t') = -\frac{1}{T^2} \left[\langle \mathcal{O}(t) \dot{x}(t') F(t') \rangle + 2 \langle \partial_x \mathcal{O}(t) v(t) \dot{x}(t') x(t') \rangle \right]. \quad (22)$$

In equilibrium $v = 0$ and $F = -\partial_x \mathcal{H}$, hence only the entropic term $-\frac{1}{T^2} \langle \mathcal{O}(t) \dot{x}(t') F(t') \rangle = \frac{1}{T^2} \frac{d}{dt'} \langle \mathcal{O}(t) \mathcal{H}(t') \rangle$ survives, and (22) correctly reduces to a Kubo formula. The nonequilibrium corrections include the correlations between the observable and the state velocity.

In conclusion, for state observables, a fluctuation-response relation to temperature changes has been derived for overdamped systems out of equilibrium, both

⁴We exploit the relations $\frac{1}{2} \frac{d^2}{dt'^2} \langle x^2(t') \mathcal{O}(t) \rangle = \langle J(t') \mathcal{O}(t) \rangle - \langle [x \dot{F}](t') \mathcal{O}(t) \rangle - 2 \langle [x x](t') [v \partial_x \mathcal{O}](t) \rangle$, $\langle \mathcal{O}(t) [F^2 - x \mathbb{L} F](t') \rangle = \langle \mathcal{O}(t) [J + x \dot{F}](t') \rangle$.

for transient conditions and for steady states generated by nonconservative forces or by temperature gradients. The understanding of the response to temperature changes complements the previous approach based on path-weights, where the response to forces was derived [13,14]. We can thus say that the picture of the linear response for nonequilibrium overdamped systems is almost complete. To fully close the circle, one needs the temperature response for systems with space-dependent noise prefactors, occurring for instance with hydrodynamic interactions or with inhomogeneous temperature fields. Investigations of these issues should consider a time rescaling, a key procedure in our approach, which leads to the concept of thermal time.

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PAPER

Nonequilibrium temperature response for stochastic overdamped systems

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G Falasco^{1,4} and M Baiesi^{2,3}¹ Max Planck Institute for Mathematics in the Sciences, Inselstr. 22, D-04103 Leipzig, Germany² Dipartimento di Fisica ed Astronomia, Università di Padova, Via Marzolo 8, I-35131 Padova, Italy³ INFN, Sezione di Padova, Via Marzolo 8, I-35131 Padova, Italy⁴ Author to whom any correspondence should be addressed.E-mail: gianmaria.falasco@mis.mpg.de and baiesi@pd.infn.it**Keywords:** non-equilibrium statistical mechanics, linear response theory, stochastic dynamics**Abstract**

The thermal response of nonequilibrium systems requires the knowledge of concepts that go beyond entropy production. This is showed for systems obeying overdamped Langevin dynamics, either in steady states or going through a relaxation process. Namely, we derive the linear response to perturbations of the noise intensity, mapping it onto the quadratic response to a constant small force. The latter, displaying divergent terms, is explicitly regularised with a novel path-integral method. The nonequilibrium equivalents of heat capacity and thermal expansion coefficient are two applications of this approach, as we show with numerical examples.

1. Introduction

The determination of response functions is arguably one of the most topical issues in statistical physics. Even though its history dates back to the works of Einstein, Nyquist and Onsager [1–4], it was Kubo [5, 6] who subsumed the later developments [7–9] under a general theory. For a system slightly driven off equilibrium, the Kubo formula gives the linear response of an observable in terms of the equilibrium time-correlation between the observable itself and the entropy produced by the perturbation. The first systematic application of Kubo's theory—along with kinetic theories based on generalised Boltzmann equations—underscored the endeavor to calculate the transport coefficients of moderately dense gasses [10]. These efforts culminated in the discovery of the algebraic decay in time of the correlation functions entering Kubo formulas [11–13], which prevents the existence of transport coefficients in low dimensions.

Later, the possibility to perform progressively more efficient computer simulations and thus to compute response functions numerically, led to the extension of the original theory to thermostatted systems arbitrarily perturbed from an initial equilibrium state [14]. Remarkably, it was established that the (nonlinear) response to an external driving is largely insensitive to the choice of the thermostating mechanisms [15], represented by the artificial forces required to maintain nonequilibrium steady-state conditions [16].

In contrast to such major achievements, the related theory for the response upon perturbation of nonequilibrium states has progressed far more slowly. Apart from the obvious obstacle represented by the lack of knowledge of nonequilibrium phase-space distributions, further difficulties are met when dealing rigorously with deterministic dynamical systems, owing to the fractal nature of their invariant distribution [17–20]. Nonequilibrium response theories have rather flourished for stochastic dynamics [21–36], which is applicable to a wide variety of complex systems in physics as well as in related sciences. However, most of these results are usually restricted to *mechanical* perturbations and do not consider *thermal* perturbations. Thus, they do not allow one to compute quantities such as nonequilibrium heat capacities and thermal expansions coefficients, which would arise as the (integrated) linear response to step variations of the temperature, i.e., of the noise intensity in the stochastic dynamical equations. Besides some previous formal results [29, 37], only recently there appeared formulas for the thermal response of driven stochastic systems, which are given in terms of

correlations between state observables calculated in the unperturbed state. Apparently, the mathematical difficulties entailed by handling noise variations require either to introduce an explicit time-discretisation to avoid divergences in the response [38, 39] or to rely on a rescaling of the stochastic dynamics in order to derive regular results [40].

The present work is devoted to show that neither of these expedients is actually necessary. A well-defined thermal response formula can be derived by standard path integral techniques, in close analogy to the case of deterministic perturbations. After introducing the model equations in section 2, we define in section 3 the linear response to a temperature perturbation of a generic observable of the system. In section 4 after a brief explanation of the formal differences from the ordinary response to a deterministic forcing, we tackle the problem first showing that the thermal response is equivalent to a portion of the quadratic (i.e. second-order) response to a constant force. Such expression, which displays divergent terms, is then explicitly regularised in section 5 and is showed to be equivalent to a Kubo formula in equilibrium. In section 6 we illustrate two applications of these results: the energy susceptibility of a driven quenched particle (that is the non-equilibrium specific heat for zero driving) and the thermal expansion coefficient of an anharmonic lattice subjected to large heat flows. Moreover, in the simplest tractable case of a freely diffusing particle we connect our formulas to the Einstein relation. A summary and an outlook are finally given in the conclusions.

2. Overdamped Langevin dynamics

The overdamped diffusive system we consider consists of N degrees of freedom, denoted $\mathbf{x} = \{x_1, \dots, x_N\}$. For instance, x_j may be a component of a particle position vector in d -dimensions, so that $N = nd$ if the system is composed by n particles. The dynamics is given by the overdamped Langevin equation

$$\dot{x}_j(t) = \mu_j F_j(\mathbf{x}(t)) + \sqrt{2\mu_j T_j} \xi_j(t), \quad (1)$$

where each Gaussian white noise ξ_j is uncorrelated from the others

$$\langle \xi_j(t) \xi_{j'}(t') \rangle = \delta(t - t') \delta_{jj'}. \quad (2)$$

The j th bath temperature T_j and mobility μ_j (which is the inverse of a damping constant) determine the strength of the noise term, while the drift depends on μ_j and on the mechanical force $F_j(\mathbf{x}(t))$. Such structure respects local detailed balance and thus assumes that the baths are noninteracting with each other and always in equilibrium, regardless of the nonequilibrium conditions experienced by the system. Temperatures and mobilities in our formalism do not depend on the coordinates, hence there is no ambiguity in the interpretation of the stochastic equation. Throughout this paper we will always consider the Stratonovich convention, that is the midpoint rule is employed to discretise in time (1) [41], which means that none of the integrals will be of the Ito type and the rules of standard calculus can be applied. See appendix A for more details.

The F_i 's are generic nonconservative forces that may bring the system arbitrarily far from equilibrium. In the resulting statistical averages, denoted $\langle \dots \rangle$, there is an understood dependence on the initial density of states $\rho_0(\mathbf{x}_0)$, with $\mathbf{x}_0 = \mathbf{x}(0)$. This may coincide or not with the steady state density. Finally, we introduce the backward generator of the Markovian dynamics (1), written as a sum of 'one-coordinate' operators \mathbb{L}_j ,

$$\mathbb{L} = \sum_{j=1}^N \mathbb{L}_j \quad \text{with} \quad \mathbb{L}_j = \mu_j F_j(\mathbf{x}) \partial_j + \mu_j T_j \partial_j^2, \quad (3)$$

where we set $\partial_{x_j} \equiv \partial_j$ to avoid clutter. It gives the average time derivative of a state observable $\mathcal{O}(t)$ as

$\frac{d}{dt} \langle \mathcal{O}(t) \rangle = \langle \mathbb{L} \mathcal{O}(t) \rangle$. Hereafter for any state observable we use the shorthand notation $\mathcal{O}(\mathbf{x}(t), t) \equiv \mathcal{O}(t)$ to indicate the implicit (and possibly explicit) dependence on the time t .

3. Linear response in path integral formalism

We imagine to perturb the system (1) varying the noise amplitude through a time dependent parameter $\theta(t) \ll 1$ switched on at time $t = 0$, namely

$$T_i \rightarrow \Theta_i(t) \equiv T_i + \epsilon_i \theta(t), \quad (4)$$

where ϵ_i is a constant determining the i th amplitude of the perturbation. This renders (1) for a perturbed degree of freedom into the form

$$\dot{x}_i(t) = \mu_i F_i(\mathbf{x}(t)) + \sqrt{2\mu_i \Theta_i(t)} \xi_i(t). \quad (5)$$

Without loss of generality we assume the mobility to be independent of temperature. The extension to the case where $\mu_i = \mu_i(\Theta_i)$ does not involve particular difficulties, since the linear response would be just the sum of the

temperature response here described plus a standard response to a deterministic perturbation [34, 35], which arises linearising the term $\mu_i F_i$.

The aim is to calculate the linear response of a generic observable $\mathcal{O}(t)$ to the just introduced temperature change, defined by

$$R_{\mathcal{O},\theta}(t, t') \equiv \frac{\delta \langle \mathcal{O}(t) \rangle_\theta}{\delta \theta(t')} \Big|_{\theta=0} = \frac{\delta}{\delta \theta(t')} \int \mathcal{D}\mathbf{x}_\theta \mathbf{d}\mathbf{x}_0 \mathcal{O}(t) P_\theta[\mathbf{x}] \rho_0(\mathbf{x}_0) \Big|_{\theta=0}. \quad (6)$$

Here $\langle \dots \rangle_\theta$ denotes an average performed in the perturbed dynamics (5) starting from the state $\rho_0(\mathbf{x}_0)$, which is unaltered by the perturbation. The associated path weight, proportional to the probability of a trajectory $[\mathbf{x}] \equiv \{\mathbf{x}(s) : 0 \leq s \leq t\}$ solution of (5), is expressed as [42]

$$P_\theta[\mathbf{x}] = \exp \mathcal{A}_\theta[\mathbf{x}], \quad (7)$$

with the action functional

$$\mathcal{A}_\theta[\mathbf{x}] = - \sum_{j=1}^N \left\{ \int_0^t ds \frac{(\dot{x}_j(s) - \mu_j F_j(s))^2}{4\mu_j \Theta_j(s)} + \frac{\mu_j}{2} \int_0^t ds \partial_j F_j(s) \right\}. \quad (8)$$

The last term in (8) appears as the functional Jacobian in deriving the path-weight for $[\mathbf{x}]$ from the Gaussian path-weight associated to the noise ξ_j , and depends on the convention used to discretise (5) (e.g. it would be absent with the Ito convention). In the following we will also make use of the unperturbed action $\mathcal{A} \equiv \mathcal{A}_{\theta=0}$, which amounts to replacing Θ_j with T_j in (8).

Deep physical insights come from separating any action of the form (8) into time-antisymmetric (\mathcal{S}) and time-symmetric (\mathcal{K} , \mathcal{K}_0) components:

$$\mathcal{A}[\mathbf{x}] = \frac{1}{2} \mathcal{S}[\mathbf{x}] - \mathcal{K}[\mathbf{x}] - \mathcal{K}_0[\mathbf{x}] \quad (9)$$

with

$$\mathcal{S}[\mathbf{x}] \equiv \sum_{j=1}^N \frac{1}{T_j} \int_0^t ds F_j(s) \dot{x}_j(s), \quad (10)$$

$$\mathcal{K}[\mathbf{x}] \equiv \sum_{j=1}^N \int_0^t ds \frac{\mu_j}{4T_j} [F_j^2(s) + 2T_j \partial_j F_j(s)], \quad (11)$$

$$\mathcal{K}_0[\mathbf{x}] \equiv \sum_{j=1}^N \int_0^t ds \frac{\dot{x}_j^2(s)}{4\mu_j T_j}. \quad (12)$$

The integrated entropy flux $\mathcal{S}[\mathbf{x}]$ is the antisymmetric part of the action \mathcal{A} under the time-reversal transformation $x_j(s) \rightarrow x_j(t-s)$. It is defined consistently with thermodynamics as the sum of the individual heat fluxes into the reservoirs, each weighted by the respective bath temperature [41]. The time-symmetric terms have been studied in connection with the notion of dynamical activity, formerly introduced in the context of jump systems [43–45], where it counts the number of jumps and provides important informations, e.g., on the state of glassy systems. Both $\mathcal{K}[\mathbf{x}]$ and $\mathcal{K}_0[\mathbf{x}]$ in fact may quantify an amount of activity in the diffusive system we are considering [46]. Being $\mathcal{K}_0[\mathbf{x}]$ related to the mean square displacement of the N degrees of freedom, it offers a direct estimate of the trajectory frenzy. Nevertheless, this kinetic-like term should be understood as part of the functional measure [42, section 2.2], as it selects from all possible trajectories the Brownian paths that make \mathcal{K}_0 finite in the limit $ds \rightarrow 0$ (i.e. those that satisfy $dx_j^2 \sim ds$). The functionals \mathcal{S} and \mathcal{K} are then the statistical weights of such selected trajectories. Therefore, in the following we will reserve the name *dynamical activity* for \mathcal{K} , which was shown to be a good measure of the system activity [46]. Written as

$$\mathcal{K}[\mathbf{x}] \equiv \int_0^t ds V_{\text{eff}}(\mathbf{x}(s)), \quad (13)$$

it may be seen as a time-integral of a state variable $V_{\text{eff}}(\mathbf{x})$ that, for systems with interactions deriving from an energy potential $U(\mathbf{x})$ and with a global bath temperature T , would read

$$V_{\text{eff}}(\mathbf{x}) = \frac{1}{4T} \sum_j \mu_j [(\partial_j U(\mathbf{x}))^2 - 2T \partial_j^2 U(\mathbf{x})]. \quad (14)$$

Such quantity was called effective potential [47, 48] and is proportional to the escape rate from a configuration \mathbf{x} , as the probability to remain in \mathbf{x} for a short time Δt is $\sim \exp(-V_{\text{eff}}(\mathbf{x})\Delta t)$. For our nonequilibrium systems we generalise such concept by writing $V_{\text{eff}}(s) = \sum_{j=1}^N \lambda_j(s)$, with

$$\lambda_j(s) \equiv \frac{\mu_j}{4T_j} [F_j^2(s) + 2T_j \partial_j F_j(s)]. \quad (15)$$

The escape rate of the degree of freedom x_j , denoted λ_j , follows from evaluating the action at fixed \mathbf{x} along a very short trajectory of duration $\Delta t \ll 1$, that is, $\lim_{\Delta t \rightarrow 0} \text{Prob}(\mathbf{x}, s + \Delta t | \mathbf{x}, s) / \Delta t = \exp\left(-\sum_{j=1}^N \lambda_j(s)\right)$.

In the following sections we will sometimes also use the name *frenesy* for describing correlation functions in the response formulas involving time-symmetrical features. This alternate naming originated in the response-theory framework [49] and usually refers to quantities akin to \mathcal{K} —more specifically, to its excess generated by a perturbing force—namely to quantities assessing the system *impatience* for changing its state (rather than direct measures of the trajectory zigzags). Hopefully the double terminology is guiding the reader through the connections with the recent literature.

4. Response to heating as response to a force

We are now in the position to develop the thermal linear response theory, but we immediately find an obstacle. Since the path weight (7) is normalised to one, $\int \mathcal{D}\mathbf{x}_\theta P_\theta[\mathbf{x}] = 1$, the functional measure $\mathcal{D}\mathbf{x}_\theta$ in (6) contains the noise temperatures Θ_j (see e.g. [42, 50]), and therefore depends itself on the external parameter θ . This is a major difference with respect to an external perturbation of the deterministic forces, which leads to the formal difficulties reported in [38], namely the introduction of an explicit time-mesh to avoid singularities in the results. To overcome this problem we first seek a more manageable expression for the path average. That is obtained through an Hubbard–Stratonovich transformation [51] of the action that, introducing an auxiliary variable \mathbf{y} , linearises the quadratic term in (8) and removes the θ dependence from the functional measure of the path weight (see e.g. [50]). By doing so, it is easy to bring (6) in the form (see appendix B)

$$\frac{\delta \langle \mathcal{O}(t) \rangle_\theta}{\delta \theta(t')} \Big|_{\theta=0} = \sum_i \frac{\epsilon_i}{\mu_i} R_{\mathcal{O}, f_i}^{(2)}(t, t', t'). \quad (16)$$

Here $R_{\mathcal{O}, f_i}^{(2)}$ is the second-order response function to a constant force perturbation f_i of the i th degree of freedom [52], namely

$$R_{\mathcal{O}, f_i}^{(2)}(t, t', t'') \equiv \frac{\delta^2 \langle \mathcal{O}(t) \rangle_f}{\delta f_i(t') \delta f_i(t'')} \Big|_{f=0}, \quad (17)$$

where $\langle \dots \rangle_f$ now denotes the average with respect to the perturbed dynamics

$$\dot{x}_i = \mu_i (F_i(\mathbf{x}) + f_i) + \sqrt{2\mu_i T_i} \xi_i. \quad (18)$$

Formal calculation of response functions to external forces poses no technical difficulty [23, 32, 34]. After integrating out the auxiliary variable \mathbf{y} , it is straightforward to find for (16)

$$\begin{aligned} R_{\mathcal{O}, f_i}^{(2)}(t, t', t') &= \frac{1}{2T_i} \frac{\delta}{\delta f_i(t')} \langle (\dot{x}_i(t') - \mu_i F_i(t') - \mu_i f_i(t')) \mathcal{O}(t) \rangle_f \Big|_{f=0} \\ &= \frac{1}{4T_i^2} [\langle (\dot{x}_i(t') - \mu_i F_i(t'))^2 \mathcal{O}(t) \rangle - 2\mu_i T_i \delta(0) \langle \mathcal{O}(t) \rangle]. \end{aligned} \quad (19)$$

Summing up, a standard Hubbard–Stratonovich transformation has allowed us to write the linear response of an observable \mathcal{O} to a temperature change as the second-order response to a state-independent force, thus arriving at the intermediate result

$$R_{\mathcal{O}, \theta}(t, t') = \sum_i \frac{\epsilon_i}{4\mu_i T_i^2} [\langle \mathcal{O}(t) (\dot{x}_i^2(t') - 2\mu_i \dot{x}_i(t') F_i(t') + \mu_i^2 F_i^2(t')) \rangle - 2\mu_i T_i \delta(0) \langle \mathcal{O}(t) \rangle]. \quad (20)$$

As anticipated, this result is slightly different from that of a previous approach [38] where the Ito convention was adopted for the path-integrals.

Let us add an alternative, intuitive mapping between linear thermal response and quadratic force response, through a less formal derivation of (16). To the purpose, it is sufficient to consider only one degree of freedom. Defining the small parameter $\mu f(t) \equiv \sqrt{2\mu\theta(t)}$ and splitting the noise into two independent, zero-mean and white Gaussian noises η and χ , equation (5) reads

$$\dot{x} = \mu F_i + \sqrt{2\mu T} \eta + \mu f \chi. \quad (21)$$

In view of equation (21), all trajectories can be regarded as generated by the noise η and perturbed by the external random force $\mu f \chi$. The corresponding response is obtained by further averaging over χ . Essentially, we wish to connect the average response to $\mu f \chi$ with the response to the deterministic force μf . We thus write the path weight associated to (21) for a single realization of χ , and expand it up to second order in the perturbing force:

$$\begin{aligned}
 P_\theta[x|\chi] &= \exp\left(-\frac{1}{4\mu T} \int_0^t ds (\dot{x} - \mu F - \mu f \chi)^2 + \frac{\mu}{2} \int_0^t ds \partial_x F\right) \\
 &\simeq P[x] \left(1 + \frac{1}{2\mu T} \int_0^t ds \mu f(s) \chi(s) (\dot{x}(s) - \mu F(s)) - \frac{1}{4\mu T} \int_0^t ds \mu f(s)^2 \chi(s)^2 \right. \\
 &\quad \left. + \frac{1}{8\mu^2 T^2} \int_0^t ds \int_0^t ds' \mu f(s) \mu f(s') \chi(s) \chi(s') (\dot{x}(s) - \mu F(s)) (\dot{x}(s') - \mu F(s'))\right). \quad (22)
 \end{aligned}$$

Recalling that $\langle \chi \rangle_\chi = 0$ and $\langle \chi(s) \chi(s') \rangle_\chi = \delta(s - s')$, averaging χ out gives

$$P_\theta[x] \simeq P[x] \left(1 - \frac{\delta(0)}{4\mu T} \int_0^t ds \mu f(s)^2 + \frac{1}{8\mu^2 T^2} \int_0^t ds \mu f(s)^2 (\dot{x}(s) - \mu F(s))^2\right). \quad (23)$$

We recognise the latter as the equal-time $O(f^2)$ term in the path weight associated to (18). So, upon application of $\delta^2/\delta f(t')^2$, it yields the quadratic force response (17) with $t' = t''$. At the same time, since $\mu f^2 = 2\theta$, the temperature response is also obtained by applying $\delta/\delta\theta(t')$ to (23), and we arrive at equality (16).

5. Regularization of the response

In (20) the divergence caused by the Dirac delta formally compensates the divergence in the squared velocity. This can be heuristically understood recalling that (20), despite being formally expressed in continuous time notation, can be interpreted in terms of discrete, albeit small, time intervals Δt [42, 53]. Therefore one has $\dot{x}_i^2 \sim 1/\Delta t$, being the dynamics diffusive at short times, and clearly $\delta(0) \sim 1/\Delta t$. However, it would be convenient to recast (20) as an explicit result devoid of singular terms. In the following we perform such operation, first for a single degree of freedom ($N = 1$), and then extending the result to arbitrary N .

5.1. One degree of freedom

With one degree of freedom the parameter ϵ_i is superfluous and is thus set to 1. We first focus on the kinetic-like term by starting with the rewriting (valid for $t > t'$)⁵

$$\langle \dot{x}^2(t') \mathcal{O}(t) \rangle = \frac{1}{2} \frac{d^2}{dt'^2} \langle x^2(t') \mathcal{O}(t) \rangle - \langle \ddot{x}(t') x(t') \mathcal{O}(t) \rangle, \quad (24)$$

and by seeking a replacement for the correlation function $\langle \ddot{x}(t') x(t') \mathcal{O}(t) \rangle$. This can be achieved recalling that the integral of a total derivative involving the path weight is null. Therefore, we may exploit the identity

$$0 = \int \mathcal{D}x \frac{\delta}{\delta x(t')} \mathcal{B}[x] P[x] = \left\langle \frac{\delta \mathcal{B}}{\delta x(t')} \right\rangle + \left\langle \mathcal{B} \frac{\delta \mathcal{A}}{\delta x(t')} \right\rangle, \quad (25)$$

where \mathcal{B} is any functional of $\{x(s) : 0 \leq s \leq t\}$, and $\mathcal{A}[x]$ is the unperturbed action

$$\mathcal{A}[x] = -\frac{1}{4\mu T} \int_0^t ds (\dot{x}(s) - \mu F(s))^2 - \frac{\mu}{2} \int_0^t ds \partial_x F(s), \quad (26)$$

corresponding to (8) calculated at $\theta = 0$, with $N = 1$. First, we evaluate the second term in (25) making use of the expression for the functional variation of the action derived in appendix C, see (C.3). The entropy variation is shown to vanish, while the variation of $\mathcal{K}[x]$ expressed in terms of the backward generator \mathbb{L} gives

$$\left\langle \mathcal{B} \frac{\delta \mathcal{A}}{\delta x(t')} \right\rangle = \left\langle \mathcal{B} \frac{\delta \mathcal{K}}{\delta x(t')} \right\rangle = \frac{1}{2\mu T} \langle \mathcal{B} [\ddot{x}(t') - \mu \mathbb{L} F(t')] \rangle. \quad (27)$$

Hereafter we restrict to the case in which F does not depend explicitly on time, but only via x . In order to extract from (27) the sought substitute for $\langle \ddot{x}(t') x(t') \mathcal{O}(t) \rangle$, we choose $\mathcal{B} = \mathcal{O}(t) x(t')$ and the first term in (25) becomes

$$\left\langle \frac{\delta \mathcal{B}}{\delta x(t')} \right\rangle = \left\langle \frac{\delta \mathcal{O}(t)}{\delta x(t')} x(t') \right\rangle + \langle \mathcal{O}(t) \rangle \delta(0). \quad (28)$$

If \mathcal{O} is a state observable, i.e., it depends only on the trajectory endpoint, the first term on the right hand side of (28) drops for all $t' \neq t$, since it reads $\frac{\delta \mathcal{O}(t)}{\delta x(t')} = \partial_x \mathcal{O}(t) \delta(t - t')$. Putting all the pieces together we get the compact expression

$$\langle \ddot{x}(t') x(t') \mathcal{O}(t) \rangle = \mu \langle \mathcal{O}(t) x(t') \mathbb{L} F(t') \rangle - 2\mu T \delta(0), \quad (29)$$

⁵ Note that average values and time derivatives commute in the Stratonovich convention [42].

which, plugged in the response formula (20), gives finally

$$R_{\mathcal{O},\theta}(t, t') = \frac{1}{4T^2} \left[\frac{1}{2\mu} \frac{d^2}{dt'^2} \langle \mathcal{O}(t)x^2(t') \rangle + \langle \mathcal{O}(t)\mu F^2(t') \rangle - \langle \mathcal{O}(t)x(t')\mathbb{L}F(t') \rangle - 2 \langle \mathcal{O}(t)\dot{x}(t')F(t') \rangle \right], \quad (30)$$

for $t' < t$. This is a regularised version of (20) valid for $N = 1$ and any state observable \mathcal{O} . We have traded the kinetic-like term and the Dirac delta in (20) with a second-order time derivative and a correlation involving the backward generator. The second-order time derivative, even though unusual for a linear response formula (but not for a second-order response function [52]), is indeed necessary to obtain the correct result, as it can be easily verified in the analytically solvable case of a particle in free diffusion (see section 6.3).

If one is interested in the response of path-dependent observables (namely, \mathcal{O} is a functional of the trajectory up to time t), the first summand in (28) is non-zero and hence (30) has to be supplemented by the term

$-2\mu T \left\langle \frac{\delta \mathcal{O}(t)}{\delta x(t')} x(t') \right\rangle$. As an example we may consider the heat exchanged with the thermal bath in a time t ,

$\mathcal{Q}[x] \equiv \int_0^t ds F(s)\dot{x}(s)$. It turns out that the response formula (30) requires no additional term in this case, since

$$\begin{aligned} \frac{\delta \mathcal{Q}(t)}{\delta x(t')} &= \partial_x F(t')\dot{x}(t') + \int_0^t ds \delta(s-t')F(s) \\ &= \partial_x F(t')\dot{x}(t') - \partial_x F(t')\dot{x}(t') = 0. \end{aligned} \quad (31)$$

5.2. Many degrees of freedom

The procedure is easily extended to a system composed of $N > 1$ degrees of freedom. Equations (24), (25) and (28) are still valid replacing x with x_i , and taking the action (corresponding to (8) calculated at $\theta = 0$)

$$\mathcal{A}[\mathbf{x}] = - \sum_{j=1}^N \left\{ \frac{1}{4\mu_j T_j} \int_0^t ds (\dot{x}_j(s) - \mu_j F_j(s))^2 + \frac{\mu_j}{2} \int_0^t ds \partial_j F_j(s) \right\}, \quad (32)$$

where we reverted to the notation accommodating the particle labels. Equation (27) is then generalised to (see appendix C)

$$\left\langle \mathcal{B} \frac{\delta \mathcal{A}}{\delta x_i(t')} \right\rangle = \frac{1}{2\mu_i T_i} \langle \mathcal{B} \ddot{x}_i(t') \rangle - \left\langle \mathcal{B} \frac{\delta \mathcal{K}}{\delta x_i(t')} \right\rangle + \frac{1}{2} \left\langle \mathcal{B} \frac{\delta \mathcal{S}}{\delta x_i(t')} \right\rangle. \quad (33)$$

In the following we focus on systems with two-body potential interactions, deferring the more general result (valid for arbitrary d , generic driving and interactions) to appendix C. Yet, the results reported here are general enough to describe the thermal response of a broad class of non-equilibrium systems, such as heat conducting lattices in contact with different heat baths (equation (38)), and aging systems (equation (40)). Under the above assumption, the variation of $\mathcal{K}[\mathbf{x}]$ in (33) is given by

$$\frac{\delta \mathcal{K}}{\delta x_i(t')} = \mathbb{L}^{(T_i)} F_i(t'), \quad (34)$$

where we identified the operator

$$\mathbb{L}^{(T_i)} \equiv \sum_{j=1}^N \frac{T_i}{T_j} \mathbb{L}_j = \sum_{j=1}^N \left(\frac{T_i}{T_j} \mu_j \partial_j + T_i \partial_j^2 \right) \quad (35)$$

which acts on the observables as if all temperatures were equal to T_i and all forces F_j were rescaled by T_i/T_j . Interesting, this rescaling is found by rewriting the Langevin dynamics in terms of a new time variable, the *thermal time* $\tau_j \equiv t \frac{T_j}{T_i}$, by which (1) reads

$$\frac{dx_j}{d\tau_j} = \mu_j \frac{T_i}{T_j} F_j + \sqrt{2\mu_j T_i} \xi_j. \quad (36)$$

While \mathbb{L} is the generator of the stochastic dynamics in the kinematic time t , in view of (36), the operator $\mathbb{L}^{(T_i)}$ acts as the generator of the corresponding dynamics in thermal time coordinates. This permits to rationalise the variation of the dynamical activity (34) as the tendency to change F_i measured with respect to the thermal time.

Coming back to the regularization of (20) we operate as before. We choose $\mathcal{B} = \mathcal{O}(t)x_i(t')$ and obtain, by means of (25), (28) and (33)

$$\langle \mathcal{O}(t)\ddot{x}_i(t')x_i(t') \rangle = \mu_i \langle \mathcal{O}(t)x_i(t')\mathbb{L}^{(T_i)} F_i(t') \rangle + \mu_i T_i \left\langle \mathcal{O}(t)x_i(t') \frac{\delta \mathcal{S}}{\delta x_i(t')} \right\rangle - 2\mu_i T_i \delta(0), \quad (37)$$

where a state observable \mathcal{O} was considered. Finally, using the explicit form of the entropy variation (C.10), we find for the response function ($t' < t$)

$$R_{\mathcal{O},\theta}(t, t') = \sum_i \frac{\epsilon_i}{4T_i^2} \left[\frac{1}{2\mu_i} \frac{d^2}{dt'^2} \langle \mathcal{O}(t)x_i^2(t') \rangle - \langle \mathcal{O}(t)x_i(t')\mathbb{L}^{(T_i)}F_i(t') \rangle + \langle \mathcal{O}(t)\mu_i F_i^2(t') \rangle - 2\langle \mathcal{O}(t)\mu_i \dot{x}_i(t')F_i(t') \rangle + \sum_{j=1}^N \langle \mathcal{O}(t)[x_i \dot{x}_j \partial_j F_i](t') \rangle \left(\frac{T_i}{T_j} - 1 \right) \right]. \quad (38)$$

This equation simplifies if the system is *isothermal* before the perturbation is applied, i.e., the heat reservoirs are all at the same temperature $T_j = T \forall j$. In this case $\frac{\delta S}{\delta x_i}$ vanishes and (33) boils down to

$$\left\langle \mathcal{B} \frac{\delta \mathcal{A}}{\delta x_i(t')} \right\rangle = \frac{1}{2\mu_i T_i} \langle \mathcal{B}[\dot{x}_i(t') - \mu_i \mathbb{L}F_i(t')] \rangle, \quad (39)$$

once we recognise $\mathbb{L}^{(T_i)}|_{T_j=T} = \sum_{j=1}^N \mathbb{L}_j$ as the total generator of the dynamics in the complete state space. Consequently, for isothermal systems the response formula takes the simpler form ($t' < t$)

$$R_{\mathcal{O},\theta}(t, t') = \frac{1}{4T^2} \sum_i \epsilon_i \left[\frac{1}{2\mu_i} \frac{d^2}{dt'^2} \langle \mathcal{O}(t)x_i^2(t') \rangle - \langle \mathcal{O}(t)x_i(t')\mathbb{L}F_i(t') \rangle + \langle \mathcal{O}(t)\mu_i F_i^2(t') \rangle - 2\langle \mathcal{O}(t)\dot{x}_i(t')F_i(t') \rangle \right], \quad (40)$$

which is a straightforward generalisation of (30) to a many-body system.

As noted above, if \mathcal{O} is a path-dependent observable one needs to include in the response formula the additional term

$$-2\mu_i T_i \left\langle \frac{\delta \mathcal{O}(t)}{\delta x_i(t')} x_i(t') \right\rangle, \quad (41)$$

coming from the first summand of (25). For the example of the total heat flux into the reservoirs, $\mathcal{Q}[\mathbf{x}] \equiv \sum_{j=1}^N \int_0^t ds F_j(s) \dot{x}_j(s)$, the supplementary term contains

$$\frac{\delta \mathcal{Q}(t)}{\delta x_i(t')} = \sum_{j=1}^N (\partial_i F_j(t') - \partial_j F_i(t')) \dot{x}_j(t'), \quad (42)$$

and thus vanishes when the interactions derive from a two-body potential.

5.3. Susceptibility

Upon integration of (38) we get an equation for the susceptibility of the system

$$\chi_{\mathcal{O},\theta}(t) \equiv \int_0^t dt' R_{\mathcal{O},\theta}(t, t') = S_1 + S_2 + K_1 + K_2 \quad (43)$$

with

$$S_1 = - \left\langle \mathcal{O}(t) \sum_i \frac{\epsilon_i}{2T_i^2} \int_0^t dt' \dot{x}_i(t') F_i(t') \right\rangle, \quad (44a)$$

$$S_2 = \left\langle \mathcal{O}(t) \sum_i \frac{\epsilon_i}{4T_i^2} \sum_{j=1}^N \left(\frac{T_i}{T_j} - 1 \right) \int_0^t dt' [x_i \dot{x}_j \partial_j F_i](t') \right\rangle, \quad (44b)$$

$$K_1 = \left\langle \mathcal{O}(t) \sum_i \frac{\epsilon_i}{4T_i^2} \int_0^t dt' [\mu_i F_i^2(t') - x_i(t') \mathbb{L}^{(T_i)} F_i(t')] \right\rangle, \quad (44c)$$

$$K_2 = \frac{d}{dt'} \left\langle \mathcal{O}(t) \sum_i \frac{\epsilon_i}{8\mu_i T_i^2} x_i^2(t') \right\rangle \Bigg|_{t'=0}^{t'=t}, \quad (44d)$$

where we recall that integrals are in the Stratonovich sense and $\mathbb{L}^{(T_i)}$ was introduced in (35). The term S_1 is the standard correlation between observable and entropy production, appearing with a $1/2$ prefactor with respect to the equilibrium version (see next section), in which it would be the only correlation relevant for determining the linear response. The term S_2 is a novel correlation between observable and a time-antisymmetric quantity, proportional to the functional variation of the bath entropy $\frac{\delta S[\mathbf{x}]}{\delta \mathbf{x}}$, which may be non-zero only if $T_j \neq T_i$ for some j . The remaining correlations, the *frenetic* terms [49] K_1 and K_2 , collect correlations between the observable

and time-symmetric dynamical features. As in previous studies of force perturbations, both S 's and K 's contain, respectively, the entropy and frenesy [49] in excess due to the perturbation.

In order to correctly evaluate the time derivative of the correlation in K_2 , when dealing with data it is important to avoid taking discrete-time derivatives with $t' > t$ because cusps are not unusual in correlation functions for $t' \rightarrow t$. To compute numerically $\frac{d}{dt'} \langle x_i^2(t') \mathcal{O}(t) \rangle |_{t'=t}$, in the examples of the following section we have estimated the slope of data for $\langle x_i^2(t') \mathcal{O}(t) \rangle$ with $t' \lesssim t$.

Only if averages are evaluated in a steady state, K_2 can be modified as

$$K_2^s = \left\langle \mathbb{L} \mathcal{O}(t) \sum_i \frac{\epsilon_i}{8\mu_i T_i^2} [x_i^2(0) - x_i^2(t)] \right\rangle \quad (44e)$$

because

$$\frac{d}{dt'} \langle \mathcal{O}(t) x_i^2(t') \rangle \Big|_{t'=0}^{t'=t} = - \frac{d}{dt} \langle \mathcal{O}(t) x_i^2(t') \rangle \Big|_{t'=0}^{t'=t} = - \langle \mathbb{L} \mathcal{O}(t) x_i^2(t') \rangle |_{t'=0}^{t'=t}. \quad (45)$$

A steady state susceptibility $\chi_{\mathcal{O},\theta}^s(t) = S_1 + S_2 + K_1 + K_2^s$ is associated with K_2^s .

5.4. A steady state formula and its reduction to the Kubo formula at equilibrium

Every thermal response formulation should reduce to the standard Kubo formula when the system is under complete equilibrium conditions at temperature T . These conditions are met if conservative forces $F_i = -\partial_i U$ (with $U(\mathbf{x})$ the system's energy) are present, if $T_i = T \forall i$ and the perturbation is applied to a thermalised system, namely $\rho_0(\mathbf{x})$ is the canonical distribution at temperature T . In equilibrium, the Kubo formula expresses the response function as

$$R_{\mathcal{O},\theta}^{\text{Kubo}}(t-t') = \frac{1}{T^2} \frac{d}{dt'} \langle \mathcal{O}(t) U(t') \rangle, \quad (46)$$

and the corresponding susceptibility is

$$\begin{aligned} \chi_{\mathcal{O},\theta}^{\text{Kubo}}(t) &= \frac{1}{T^2} \langle \mathcal{O}(t) [U(t) - U(0)] \rangle, \\ &= \frac{1}{T^2} \langle \mathcal{O}(t) \mathcal{Q}(t) \rangle, \end{aligned} \quad (47)$$

where $\mathcal{Q}(t) = U(t) - U(0)$ is the heat transferred to the system in the time interval $[0, t]$. This formula shows that the temperature response in equilibrium is totally determined by the correlation between observable and the entropy $\mathcal{Q}(t)/T$ paid by the reservoir to change the system energy.

When a global perturbation is applied to an isothermal steady state regime, say with $\epsilon_i = 1 \forall i$, equation (40) may be recast in an alternative form, that correctly reduces to the Kubo formula (46) in equilibrium, as we show in the following. In the derivation we stay in a generic steady state condition until the very end, so that in turn we obtain another quite general formula for the response function, equation (51) below, in which the genuine nonequilibrium contribution is well distinguished from the Kubo correlation. A possible practical issue of such elegant separation is that it can be computed explicitly only if one knows the microscopic probability density of states.

We start noticing that the last term in (40) is in equilibrium half of the expected result:

$$\frac{1}{2T^2} \sum_i \langle \mathcal{O}(t) \dot{x}_i(t') \partial_i U(t') \rangle = \frac{1}{2T^2} \frac{d}{dt'} \langle \mathcal{O}(t) U(t') \rangle. \quad (48)$$

The remaining frenetic terms yield an analogous contribution at equilibrium. To show that, we first use that the system is in a stationary state. This implies that correlations are functions of the time difference only, hence $\frac{d}{dt'}$ can be exchanged with $-\frac{d}{dt}$. Moreover, the backward generator can be expressed in terms of the generator of the time-reversed dynamics, \mathbb{L}^* , through the relation $\mathbb{L} = \mathbb{L}^* + 2\sum_{j=1}^N v_j \partial_j$, where $v_j \equiv J_j^s / \rho^s$ is the state velocity, that is the probability current J_j^s associated to x_j , over the steady state density of the system ρ^s [49, 54]. We will ultimately exploit the time-reversal invariance of equilibrium states, which formally manifests in the equality $\mathbb{L} = \mathbb{L}^*$, as the probability currents v_j are by definition absent at equilibrium.

The time derivatives in (40) can be manipulated as

$$\begin{aligned}
\frac{1}{2\mu_i} \frac{d^2}{dt'^2} \langle x_i^2(t') \mathcal{O}(t) \rangle &= -\frac{1}{2\mu_i} \frac{d}{dt'} \frac{d}{dt} \langle x_i^2(t') \mathcal{O}(t) \rangle \\
&= -\frac{1}{2\mu_i} \frac{d}{dt'} \langle x_i^2(t') \mathbb{L} \mathcal{O}(t) \rangle \\
&= -\frac{1}{2\mu_i} \frac{d}{dt'} \left\langle x_i^2(t') \left(\mathbb{L}^* + 2 \sum_j v_j \partial_j \right) \mathcal{O}(t) \right\rangle \\
&= -\frac{1}{2\mu_i} \frac{d}{dt'} \left[\langle (\mathbb{L} x_i^2(t')) \mathcal{O}(t) \rangle + 2 \sum_j \langle x_i^2(t') v_j \partial_j \mathcal{O}(t) \rangle \right] \\
&= -\frac{d}{dt'} \left[\langle x_i(t') F_i(t') \mathcal{O}(t) \rangle + \frac{1}{\mu_i} \sum_j \langle x_i^2(t') v_j \partial_j \mathcal{O}(t) \rangle \right]. \tag{49}
\end{aligned}$$

Together with stationarity, we used that \mathbb{L}^* is the adjoint of \mathbb{L} , and the equality $\mathbb{L} x_i^2 = 2\mu_i F_i x_i + \text{const}$ in the last passage. We then turn to the second and third summand in (40), starting with the rewriting $\mu_i F_i^2 = F_i \mathbb{L} x_i$:

$$\begin{aligned}
\langle \mathcal{O}(t) (F_i(t') \mathbb{L} x_i(t') - x_i(t') \mathbb{L} F_i(t')) \rangle &= \langle \mathcal{O}(t) (F_i(t') [\mathbb{L}, x_i](t') - x_i(t') [\mathbb{L}, F_i](t')) \rangle \\
&= -\langle \mathcal{O}(t) (F_i(t') \dot{x}_i(t') - x_i(t') \dot{F}_i(t')) \rangle. \tag{50}
\end{aligned}$$

Here we introduced the commutator acting as, e.g., $[x_i, \mathbb{L}] \equiv x_i \mathbb{L} - \mathbb{L} x_i$, and exploit the fact that in the operator formalism time derivatives within average values are given by $\dot{\mathcal{O}} = [\mathcal{O}, \mathbb{L}]$, for any state observable \mathcal{O} (see appendix D). Putting together equations (48), (49) and (50) we obtain an expression of the thermal response valid under stationary isothermal conditions

$$R_{\mathcal{O},\theta}(t, t') = -\frac{1}{T^2} \sum_i \left[\langle \mathcal{O}(t) \dot{x}_i(t') F_i(t') \rangle + \frac{1}{4\mu_i} \frac{d}{dt'} \left\langle \sum_j v_j(t) \partial_j \mathcal{O}(t) x_i^2(t') \right\rangle \right]. \tag{51}$$

Finally, at equilibrium the Kubo formula (46) is retrieved by setting $v_j = 0 \forall j$ and using the rewriting (48) for potential forces. Equation (51) is a thermal response counterpart of previous results for the steady-state force response based on the notion of state velocity [26, 27].

6. Examples

6.1. Specific heat for a quenched toy system

In this first example we want to highlight that this framework is valid not only for steady states but also for transient regimes. There is to recall an understood dependence of the statistical averages $\langle \dots \rangle$ on the initial density of states ρ_0 .

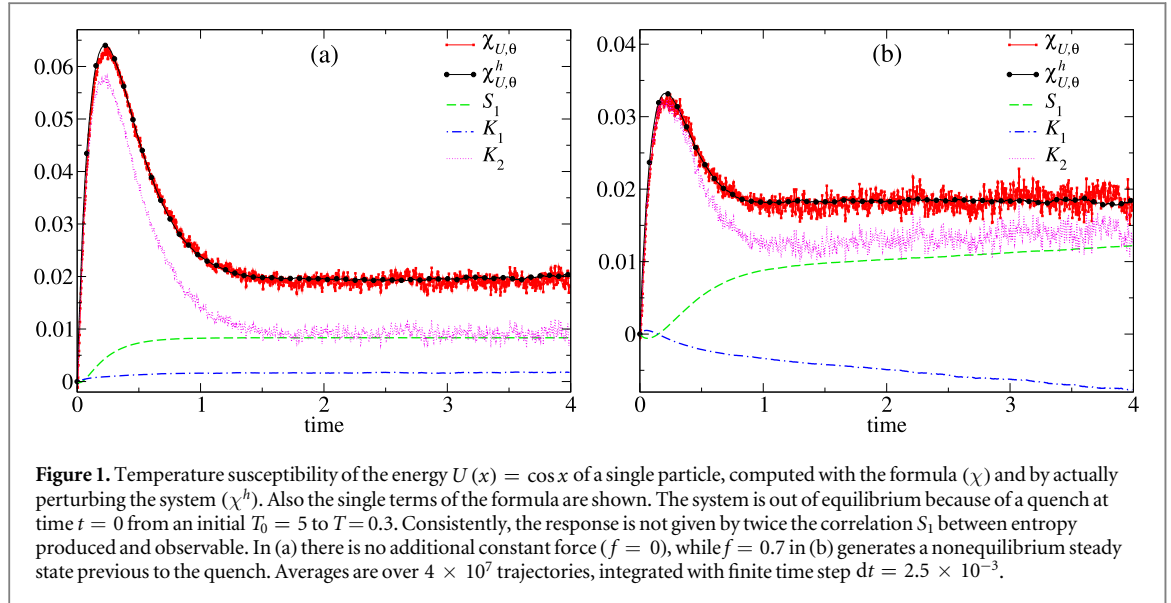
Let us consider a paradigmatic model of nonequilibrium overdamped systems, namely a single particle in a periodic potential $U(x) = \cos x$ and subject to an additional constant force f , for simplicity with mobility $\mu = 1$. Thus $F(x) = \sin x + f$, in the evolution equation (1) of the unperturbed system. The backward operator acts on the force as $\mathbb{L} F(x) = \sin x \cos x - T \sin x$.

To generate a transient condition we choose to thermalise the particle at $T_0 \neq T$ and to switch to T only at $t = 0$, when the perturbation is also applied. In this way, even for $f = 0$ one cannot apply the Kubo formula for equilibrium systems, as the initial state is not in equilibrium at temperature T . Due to the periodic potential, as an arbitrary procedure for obtaining a well defined $\rho_0(x)$, we shift to the interval $[0, 2\pi]$ any x obtained from a long simulation run. However, averages such as $\langle x^2(t') \mathcal{O}(t) \rangle$ need to be computed with x interpreted as a non-periodic coordinate. We adopted a Heun scheme [41] to integrate the stochastic equation, because it yields trajectories that are consistent with the Stratonovich path-weights used in our theory.

In figure 1 we show examples of susceptibilities of the internal energy ($\mathcal{O} = U$) to a change of T for $T_0 = 5$ and $T = 0.3$, both for $f = 0$ and $f = 0.7$. We compare the susceptibility $\chi_{U,\theta}(t)$ from (43) with that computed directly as

$$\chi_{U,\theta}^h(t) = \frac{\langle U(t) \rangle_{\theta=h} - \langle U(t) \rangle_{\theta=0}}{h} \tag{52}$$

with $h = T/100$ active from $t = 0$ on. We note that, for $f = 0$, the force F is potential and thus the heat exchanged with the bath reduces to an energy difference, $\mathcal{Q} = -\int_0^t dt' \partial_x U(t') \dot{x}(t') = U(0) - U(t)$. Therefore, the susceptibility of the energy gives in the long-time limit the specific heat C of the system:



$$C \equiv -\lim_{t \rightarrow \infty} \int_0^t dt' \frac{\delta \langle Q(t) \rangle_\theta}{\delta \theta(t')} \Big|_{\theta=0} = \lim_{t \rightarrow \infty} \chi_{U,\theta}(t). \quad (53)$$

If a Kubo formula (46) were valid, twice the entropic term (44a) would yield the response. One can note that this is not the case, rather all terms in the response formula are relevant for determining the correct form of the susceptibility. In these examples, in particular, the term (44d) is especially important. Being the derivative of a correlation function, it is however the noisiest one. One could resort to some high-frequency filtering for better results. In the example of the following subsection we will show that (44e) is a good alternative to (44d) in case one is dealing with steady states.

6.2. Thermal expansion in a temperature gradient

In equilibrium at a given temperature T , the correlation function between the heat absorbed by a system and its length may be used to predict the thermal expansion response. In this example we show how this picture breaks down out of equilibrium, where, as exposed in the previous sections, one needs to know also correlations between length and time-symmetric observables, given by (44c) and (44d) or (44e), as well as the new entropic form (44b) due to temperature unbalances. This example specialises to steady state conditions but, with respect to the previous examples, it includes the more general setup of multiple heat baths, in which one can exploit the general formulation with perturbation amplitudes ϵ_i .

Let us consider the N degrees of freedom arranged in a one-dimensional chain. The system has an energy

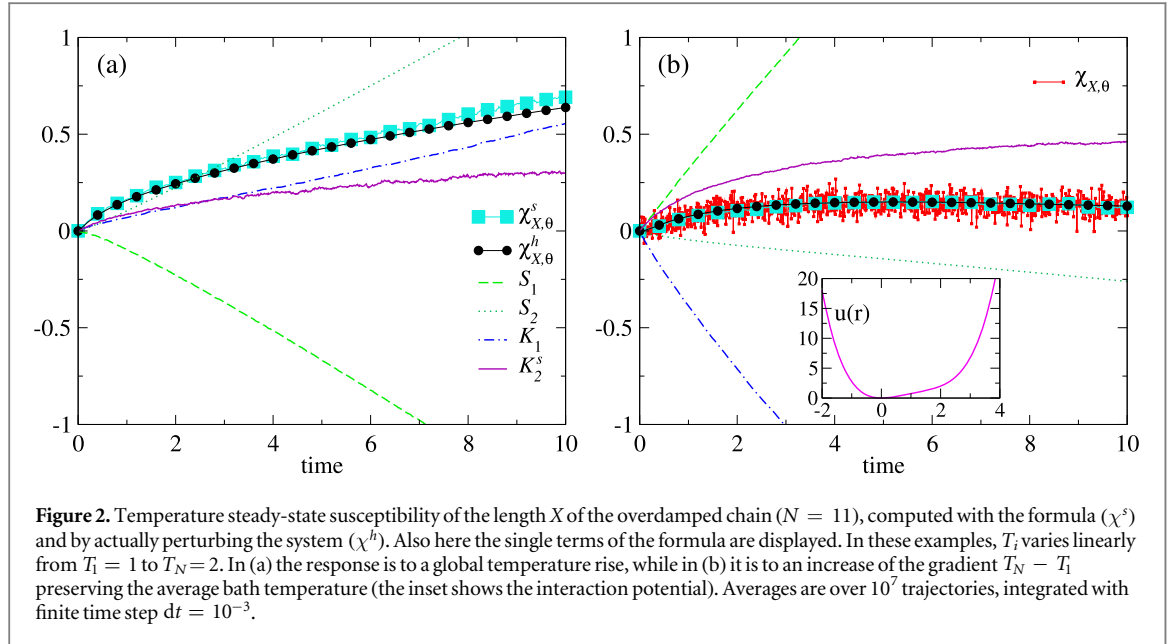
$$U(\mathbf{x}) = \frac{x_1^2}{2} + \sum_{i=1}^{N-1} u(x_{i+1} - x_i), \quad \text{with} \quad u(r) = \frac{(r-1)^4}{4} + r - \frac{1}{4} \quad (54)$$

which determines the forces, $F_i(\mathbf{x}) = -\partial_i U(\mathbf{x})$, and again mobilities μ_i are set equal to 1 for simplicity. The $x_1^2/2$ term is a pinning potential on the first site, and x_i 's represent the displacements from the average positions. The length of the system in excess with respect to the length at zero temperature, $X \equiv x_N - x_1$, increases on average for increasing T_i 's due to the asymmetric two-body potential $u(r)$ (see the inset of figure 2(b)). As a paradigm of nonequilibrium conditions, the system is driven by a set of temperatures varying linearly from T_1 to $T_N > T_1$.

We study the response of the length X to temperature variations, in the form of (a) a global constant increase of the temperatures given by a constant $\epsilon_i = 1$, and (b) an increment of the gradient $T_N - T_1$, chosen so that the average temperature is unaltered by varying ϵ_i linearly from $\epsilon_1 = -1$ to $\epsilon_N = 1$. For both cases, in figure 2 we see that the susceptibility $\chi_{X,\theta}^s$ computed with the steady state term (44e) agrees fairly well with the direct estimate of the response

$$\chi_{X,\theta}^h(t) = \frac{\langle X(t) \rangle_{\theta=h} - \langle X(t) \rangle_{\theta=0}}{h}, \quad (55)$$

obtained with a constant $h = 0.005$ turned on at $t = 0$. From figure 2 one also sees that the entropic and frenetic terms have opposite trends, between each other and with switched roles in the two cases, complementing each other to sum up to the correct response level. In figure 2(b) we also show the response $\chi_{X,\theta}$ obtained by an



evaluation of the time-derivative in (44d) (the local variation in time of the correlation function is obtained through a linear fit of data relative to four nearby time steps). It results more noisy than the estimate via $\chi_{X,\theta}^s$.

6.3. Free diffusion of one degree of freedom

Let us consider the equations of motion (1) for free diffusion of a single degree of freedom, $\dot{x}(t) = \hat{\xi}(t)$ with $\hat{\xi} = \sqrt{2\mu T}\xi$. The noise prefactor $\sqrt{2\mu T}$ comes from assuming the bath to be in equilibrium. In this way the mean square displacement of a free particle in a time t is simply $\langle x^2(t) \rangle = 2\mu Tt \equiv 2Dt$, the response of the mean velocity to a small force is the free-particle mobility μ , and the Einstein relation $\mu = D/T$ between diffusion constant D and mobility is found. One can note that the susceptibility of the observable $\mathcal{O}(t) = x^2(t)$ to a change of T is expected to be $2\mu t$, hence the corresponding response function is 2μ . We show how our formalism reduces to this result.

For free diffusion all terms in (30) drop but the one involving the second derivative. In this case, the response function can be calculated directly from its definition (6) and one can thus prove analytically that both sides of (30) are equal to the same quantity. As we argued above, the response of the mean square displacement to the perturbation $T \rightarrow \Theta(t) = T + \theta(t)$ is

$$\begin{aligned} \frac{\delta \langle x^2(t) \rangle_h}{\delta \theta(t')} &= \frac{\delta}{\delta \theta(t')} \left\langle x_0^2 + 2x_0 \int_0^t ds \hat{\xi}(s) + \int_0^t ds \int_0^t du \hat{\xi}(s) \hat{\xi}(u) \right\rangle \\ &= 2\mu \frac{\delta}{\delta \theta(t')} \int_0^t ds \int_0^t du \delta(s-u) \Theta(s) \\ &= 2\mu. \end{aligned} \quad (56)$$

Here we used that the initial condition is independent of the perturbation and noise, thus only the noise autocorrelation contributes. On the other hand, the response formula (30) becomes

$$\begin{aligned} R_{x^2 T}(t, t') &= \frac{1}{8\mu T^2} \frac{d^2}{dt'^2} \langle x^2(t') x^2(t) \rangle \\ &= \frac{1}{8\mu T^2} \frac{d^2}{dt'^2} (\langle x^2(t') \rangle \langle x^2(t) \rangle + 2 \langle x(t') x(t) \rangle^2), \end{aligned} \quad (57)$$

making use of Wick's theorem to split the four-point correlation into products of two-point correlations. The latter read

$$\langle x(t') x(t) \rangle = \langle x_0^2 \rangle + \int_0^{t'} ds \int_0^t du \langle \xi(s) \xi(u) \rangle = \langle x_0^2 \rangle + 2\mu T \min(t', t), \quad (58)$$

leading to a result in agreement with the previous calculation:

$$\begin{aligned}
 R_{x^2T}(t, t') &= \frac{1}{8\mu T^2} \frac{d^2}{dt'^2} [(\langle x_0^2 \rangle + 2\mu T t')(\langle x_0^2 \rangle + 2\mu T t) + 2(\langle x_0^2 \rangle + 2\mu T t')^2] \\
 &= \frac{1}{8\mu T^2} \frac{d^2}{dt'^2} [3\langle x_0^2 \rangle^2 + 2\mu T \langle x_0^2 \rangle (t' + t) + (2\mu T)^2 t t' + 8\mu T t' \langle x_0^2 \rangle + 2(2\mu T)^2 t'^2] \\
 &= 2\mu.
 \end{aligned} \tag{59}$$

As expected, interchanging $\frac{d}{dt^2}$ with $\frac{d}{dt'^2}$ would give an incorrect result as the system is not in a steady state. It is also trivial to verify (16), namely that this result coincides with the second order response to a state-independent force, giving rise to the dynamics $\dot{x}(t) = \mu f(t) + \hat{\xi}(t)$. Indeed, using again the conditions of independency of the initial condition, one finds

$$\begin{aligned}
 \frac{1}{\mu} \frac{\delta^2 \langle x^2(t) \rangle_f}{\delta f^2(t')} &= \frac{1}{\mu} \frac{\delta^2}{\delta f^2(t')} \left\langle \left(\int_0^t ds (\mu f(s) - \hat{\xi}(s)) \right)^2 \right\rangle \\
 &= \mu \frac{\delta^2}{\delta f^2(t')} \int_0^t ds \int_0^t du f(s) f(u) \\
 &= 2\mu.
 \end{aligned} \tag{60}$$

7. Conclusions

For overdamped stochastic systems far from equilibrium we have obtained the linear response function of generic state observables to a change in the temperature of the Langevin heat baths. Improving a previous result [38], we need not express the response in terms of a finite time mesh, being all the divergencies appearing in the continuous limit removed, and being all terms in the susceptibility standard integrals or derivatives. This was achieved by deriving a sort of Dyson–Schwinger equation [42], i.e., a relation between unperturbed correlation functions involving an arbitrary observable. This method complements and expands our recent results [40] obtained via a different approach, in which the additional noise stemming from the perturbation was turned into mechanical forces by means of a space rescaling.

As in many previous examples, in order to describe a nonequilibrium systems, one needs to know more than just the entropy production. The additional information concerns the knowledge of dynamical quantities that are even under the reversal of the arrow of time (squares of forces, etc). Among them we have recognised the change of the time-integral of the effective potential (i.e., the total escape rate integrated along trajectories) upon variation of the perturbed degree of freedom, $\frac{\delta \mathcal{K}}{\delta x_i}$. This quantity emerges from the regularization procedure we set up, along with the change of the total bath entropy flow $\frac{\delta \mathcal{S}}{\delta x_i}$, which complements, perhaps surprisingly, the usual entropy production entering Kubo formula.

For the common scenario of isothermal systems in a steady state, we have also shown how to convert the results in a formula that separates the Kubo term from a nonequilibrium additional correlation that includes the state velocity, see (51). Such version is complementary to the others in the sense that it requires the knowledge of the density of states rather than that of dynamical details.

Future developments of this framework should include multiplicative noise, i.e. those cases where the temperature experienced by the particle depends on their positions.

Appendix A. Stochastic convention for path weights

In this context of temperature response, even if equations have a noise prefactor that does not depend on the system's state \mathbf{x} , it turns out that the choice of using Stratonovich path-weights rather than Ito ones is not trivial. As discussed previously [39], by differentiating with respect to temperature one proves a response formula that depends on the choice of the path-weight. One can check that the formulas in this paper are indeed different from those found adopting the Ito convention [38]. The adoption of the Stratonovich convention in the path weight (8) is reflected in the Stratonovich product $\dot{x}F$ in (20). If we used an Ito convention in (8), then $\dot{x}F$ in (20) would also be of the Ito type and the same equation would not match the result obtained in the Stratonovich convention.

Ultimately, the path-weight, and thus the corresponding discretisation of (1), have to be chosen consistently with the process that generates the sampled trajectory via (1). By sampled trajectory we mean for example a sequence $\{\mathbf{x}(0), \mathbf{x}(\Delta t), \mathbf{x}(2\Delta t), \dots, \mathbf{x}(t - \Delta t), \mathbf{x}(t)\}$ of configurations sampled stroboscopically every time step Δt . The Ito convention is by construction suitable for numerical data generated by integration of (1) with

Euler scheme with step Δt [38]. On the other hand, the Wong–Zakai theorem [55] ensures the Stratonovich convention to be adequate to experimental data, for which the white noise is an idealised limit of the short correlation times of the microscopic degrees of freedom.

Appendix B. Derivation of the second order response function

The derivation of (16) starts with a Hubbard–Stratonovich transformation of the path weight, which is a functional generalisation of the integral identity $\int dy e^{-Dy^2 - izy} = e^{-\frac{z^2}{4D}} \sqrt{\frac{\pi}{D}}$ (below the $\sqrt{\pi/D}$ is adsorbed in the path measure $\mathcal{D}y$) valid for real y and $D > 0$. When applied to (7) and (8) it renders the response (6) in the form (16) through the following manipulations:

$$\begin{aligned} \frac{\delta \langle \mathcal{O}(t) \rangle_\theta}{\delta \theta(t')} \Big|_{\theta=0} &= \frac{\delta}{\delta \theta(t')} \int \mathcal{D}\mathbf{x} d\mathbf{x}_0 \mathcal{D}y \rho_0(\mathbf{x}_0) \mathcal{O}(t) \\ &\quad \times \prod_{j=1}^N \exp \left\{ - \int_0^t ds \left[\mu_j \Theta_j y_j^2 - iy_j (\dot{x}_j - \mu_j F_j) + \frac{1}{2} \mu_j \partial_j F_j \right] \right\} \Big|_{\theta=0} \\ &= \int \mathcal{D}\mathbf{x} d\mathbf{x}_0 \mathcal{D}y \rho_0(\mathbf{x}_0) \mathcal{O}(t) \left[- \sum_i \epsilon_i \mu_i y_i^2(t') \right] \\ &\quad \times \prod_{j=1}^N \exp \left\{ - \int_0^t ds \left[\mu_j T_j y_j^2 - iy_j (\dot{x}_j - \mu_j F_j) + \frac{1}{2} \mu_j \partial_j F_j \right] \right\}, \end{aligned} \quad (\text{B.1})$$

$$\begin{aligned} &= \sum_i \frac{\epsilon_i}{\mu_i} \frac{\delta^2}{\delta f_i^2(t')} \int \mathcal{D}\mathbf{x} d\mathbf{x}_0 \mathcal{D}y \rho_0(\mathbf{x}_0) \mathcal{O}(t) \\ &\quad \times \prod_{j=1}^N \exp \left\{ - \int_0^t ds \left[\mu_j T_j y_j^2 - iy_j (\dot{x}_j - \mu_j F_j - \mu_j f_j) + \frac{1}{2} \mu_j \partial_j F_j \right] \right\} \Big|_{f=0} \\ &= \sum_i \frac{\epsilon_i}{\mu_i} R_{\mathcal{O}, f_i}^{(2)}(t, t', t'), \end{aligned} \quad (\text{B.2})$$

where we rewrote (B.1) introducing the derivatives of a state-independent force f_i , and recognised in (B.2) the Martin–Siggia–Rose path-weight [56] associated to the perturbed dynamics (18).

Appendix C. Variation of the action functional

Here we detail the calculation of the functional variation of the path-weight action $\mathcal{A}[\mathbf{x}]$ that was used in section 5. For the sake of clarity we distinguish the single-particle from the many-particle case.

C.1. One degree of freedom

For $N = 1$, the action is given by (26) and its variation is

$$\frac{\delta \mathcal{A}}{\delta x(t')} = \frac{1}{2} \frac{\delta \mathcal{S}}{\delta x(t')} - \frac{\delta \mathcal{K}}{\delta x(t')} + \frac{\ddot{x}(t')}{2\mu T}. \quad (\text{C.1})$$

The variation of the bath entropy is identically zero, unless F is an explicit function of time $F(t') = F(x(t'), t')$:

$$\begin{aligned} \frac{\delta \mathcal{S}}{\delta x(t')} &= \frac{1}{T} \left(\partial_x F(t') \dot{x}(t') + \int_0^t ds \delta(s - t') F(s) \right) \\ &= \frac{1}{T} (\partial_x F(t') \dot{x}(t') - \partial_{t'} F(t') - \partial_x F(t') \dot{x}(t')) = -\frac{1}{T} \partial_{t'} F(t'). \end{aligned}$$

Since the dynamical activity is independent of \dot{x} , its variation is simply the derivative of the escape rate from $x(t')$:

$$\frac{\delta \mathcal{K}}{\delta x(t')} = \partial_x \lambda(t') = \frac{1}{2T} (\mu F(t') \partial_x F(t') - \mu T \partial_x^2 F(t')). \quad (\text{C.2})$$

Therefore, introducing in (C.2) the backward generator \mathbb{L} , (C.1) becomes

$$\frac{\delta \mathcal{A}}{\delta x(t')} = \frac{1}{2\mu T} [\ddot{x}(t') - \mu \mathbb{L} F(t') - \mu \partial_{t'} F(t')]. \quad (\text{C.3})$$

As a side note, plugging this result into (25) with $\mathcal{B} = 1$ one obtains (if F depends on x only)

$$\langle \ddot{x} \rangle = \mu \langle \mathbb{L}F \rangle, \quad (\text{C.4})$$

i.e., the mean trajectory satisfies Newton's equation with an effective force $\mu \mathbb{L}F$. In the weak-noise limit $T \ll 1$, such trajectory becomes the most probable one, being the minimiser of the action. This expression could be obtained directly by applying the backward generator \mathbb{L} to the Langevin equation (1), and using that ξ does not depend on x .

C.2. Many degrees of freedom

For $N > 1$, thanks to the independency of the different thermal noises, the action (32) is simply the sum of 'single-coordinate' actions: $\mathcal{A}[\mathbf{x}] = \sum_{j=1}^N \mathcal{A}^{(j)}[\mathbf{x}]$ with $\mathcal{A}^{(j)}$ following the structure (26). Nevertheless, its variation is not just equal to (C.3) but in general it will contain additional terms owing to the interactions between different degrees of freedom. One indeed finds modified expressions for the variation of the total entropy flux into the (unperturbed) reservoirs

$$\frac{\delta \mathcal{S}[\mathbf{x}]}{\delta x_i(t')} = \sum_{j=1}^N \dot{x}_j(t') \left(\frac{\partial_i F_j(t')}{T_j} - \frac{\partial_j F_i(t')}{T_i} \right) - \frac{1}{T_i} \partial_{t'} F_i(t'), \quad (\text{C.5})$$

and for the variation of the total dynamical activity

$$\frac{\delta \mathcal{K}}{\delta x(t')} = \sum_{j=1}^N \partial_i \lambda_j(t') = \sum_{j=1}^N \frac{1}{2T_j} (\mu_j F_j(t') \partial_i F_j(t') + \mu_j T_j \partial_i \partial_j F_j(t')), \quad (\text{C.6})$$

which in general cannot be cast in terms of the total backward generator \mathbb{L} . The variation of the action is thus given by

$$\begin{aligned} \frac{\delta \mathcal{A}}{\delta x_i(t')} &= \frac{1}{2} \frac{\delta \mathcal{S}}{\delta x_i(t')} - \frac{\delta \mathcal{K}}{\delta x_i(t')} + \frac{\ddot{x}_i(t')}{2\mu_i T_i} \\ &= \frac{1}{2\mu_i T_i} \left[\ddot{x}_i(t') - \mu_i T_i \sum_{j=1}^N \partial_i \lambda_j(t') - \mu_i \partial_{t'} F_i(t') \right. \\ &\quad \left. + \mu_i T_i \sum_{j=1}^N \dot{x}_j(t') \left(\frac{\partial_i F_j(t')}{T_j} - \frac{\partial_j F_i(t')}{T_i} \right) \right]. \end{aligned} \quad (\text{C.7})$$

Equation (C.7) is completely general, and thus, when combined with (33), provides a regularised expression for the thermal response of overdamped systems under any nonequilibrium conditions:

$$\begin{aligned} R_{\mathcal{O},\theta}(t, t') &= \sum_i \frac{\epsilon_i}{4T_i^2} \left[\frac{1}{\mu_i} \frac{d^2}{dt'^2} \langle \mathcal{O}(t) x_i^2(t') \rangle - \langle \mathcal{O}(t) x_i(t') \partial_{t'} F_i(t') \rangle \right. \\ &\quad \left. + \left\langle \mathcal{O}(t) \left(\mu_i F_i^2(t') - 2\dot{x}_i(t') F_i(t') - x_i(t') T_i \sum_{j=1}^N \partial_i \lambda_j(t') \right) \right\rangle \right] \\ &\quad \left. + T_i \sum_{j=1}^N \left\langle \mathcal{O}(t) x_i(t') \dot{x}_j(t') \left(\frac{\partial_i F_j(t')}{T_j} - \frac{\partial_j F_i(t')}{T_i} \right) \right\rangle \right]. \end{aligned} \quad (\text{C.8})$$

Nevertheless, the cross-terms $\partial_i F_j$ with $i \neq j$ appearing in (C.7) simplify considerably if we assume that the degrees of freedom interact with each others via a two-body potential $\mathcal{U}(\{x_i - x_j\})$. Hence we can exploit the relation

$$\partial_i F_j = -\partial_i \partial_j \mathcal{U} = -\partial_j \partial_i \mathcal{U} = \partial_j F_i, \quad (\text{C.9})$$

which is nothing but the action-reaction principle. Equation (C.7) then becomes

$$\frac{\delta \mathcal{A}}{\delta x_i(t')} = \frac{1}{2\mu_i T_i} [\ddot{x}_i(t') - \mu_i \mathbb{L}^{(T_i)} F_i(t') - \mu_i \partial_{t'} F_i(t')] + \sum_{j=1}^N \dot{x}_j(t') \partial_j F_i(t') \left(\frac{1}{2T_j} - \frac{1}{2T_i} \right). \quad (\text{C.10})$$

We remark that for systems in $d = 1$ (C.9) does not impose any limitation on the driving, that is, one-body non-conservative forces can be present as well, they simply do not enter in (C.7), which concerns only the interactions between different particles. Instead, in $d > 1$, different indexes i and j in (C.7) may refer to the coordinates of the same particle, thus (C.7) cannot be simplified to (C.10) in the presence of generic non-conservative forces.

It is worth noting that when the equality $\partial_i F_j = \partial_j F_i$ holds, the choice $\mathcal{B} = 1$ in the identity (25) yields the effective Newton's equation for the mean trajectory

$$\langle \dot{x}_i \rangle = \mu_i \langle \mathbb{L}^{(T)} F_i \rangle - \mu_i T_i \left\langle \frac{\delta \mathcal{S}}{\delta x_i} \right\rangle. \quad (\text{C.11})$$

On the other hand, direct application of the operator \mathbb{L} to the Langevin equation (1) gives $\langle \dot{x}_i \rangle = \mu_i \langle \mathbb{L} F_i \rangle$. By comparison, one concludes that there exists a natural splitting of the effective force, namely

$$\langle \mathbb{L} F_i \rangle = \mu_i \langle \mathbb{L}^{(T)} F_i \rangle - \mu_i T_i \left\langle \frac{\delta \mathcal{S}}{\delta x_i} \right\rangle, \quad (\text{C.12})$$

where the first component originates from variations of the force F_i in thermal time, while the second is a gradient-like force in which the entropy flux into the bath acts a free-energy.

Appendix D. Time derivative in operator formalism

Consider the state observables \mathcal{O}_α , that are arbitrary functions of \mathbf{x} . In the operator formalism, their (steady-state) evolution over a time-span $t - t'$ is given by the action of the operator $e^{-\mathbb{L}(t-t')}$. Therefore, the typical correlation functions we are interested in are expressed by (with $t > t'$)

$$\langle \mathcal{O}_3(t) \mathcal{O}_2(t') \mathcal{O}_1(t') \rangle = \int d\mathbf{x}_0 \rho_0(\mathbf{x}_0) e^{\mathbb{L}t'} \mathcal{O}_1 \mathcal{O}_2 e^{-\mathbb{L}(t-t')} \mathcal{O}_3, \quad (\text{D.1})$$

where the dependence of \mathcal{O}_α on \mathbf{x}_0 is omitted for brevity [49]. In analogy to the Heisenberg picture in quantum mechanics, one may include the dependency on time in the observables by the definition $\mathcal{O}_\alpha(t') \equiv e^{\mathbb{L}t'} \mathcal{O}_\alpha e^{-\mathbb{L}t'}$. Hence, a time derivative applied to one of the operators in (D.1) gives, e.g.

$$\begin{aligned} \langle \mathcal{O}_3(t) \dot{\mathcal{O}}_2(t') \mathcal{O}_1(t') \rangle &= \langle \mathcal{O}_3(t) (\mathbb{L} e^{\mathbb{L}t'} \mathcal{O}_2 e^{-\mathbb{L}t'} - e^{\mathbb{L}t'} \mathcal{O}_2 e^{-\mathbb{L}t'} \mathbb{L}) \mathcal{O}_1(t') \rangle \\ &= \langle \mathcal{O}_3(t) (\mathbb{L} \mathcal{O}_2(t') - \mathcal{O}_2(t') \mathbb{L}) \mathcal{O}_1(t') \rangle \\ &= \langle \mathcal{O}_3(t) [\mathbb{L}, \mathcal{O}_2(t')] \mathcal{O}_1(t') \rangle. \end{aligned} \quad (\text{D.2})$$

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Thermal response of nonequilibrium RC circuitsMarco Baiesi,^{1,2,*} Sergio Ciliberto,³ Gianmaria Falasco,^{4,5} and Cem Yolcu^{1,†}¹*Department of Physics and Astronomy, University of Padova, Via Marzolo 8, I-35131 Padova, Italy*²*INFN, Sezione di Padova, Via Marzolo 8, I-35131 Padova, Italy*³*Laboratoire de Physique de Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, 69364 Lyon, France*⁴*Max Planck Institute for Mathematics in the Sciences, Inselstr. 22, 04103 Leipzig, Germany*⁵*Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, D-04009 Leipzig, Germany*

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We analyze experimental data obtained from an electrical circuit having components at different temperatures, showing how to predict its response to temperature variations. This illustrates in detail how to utilize a recent linear response theory for nonequilibrium overdamped stochastic systems. To validate these results, we introduce a reweighting procedure that mimics the actual realization of the perturbation and allows extracting the susceptibility of the system from steady-state data. This procedure is closely related to other fluctuation-response relations based on the knowledge of the steady-state probability distribution. As an example, we show that the nonequilibrium heat capacity in general does not correspond to the correlation between the energy of the system and the heat flowing into it. Rather, also nondissipative aspects are relevant in the nonequilibrium fluctuation-response relations.

DOI: [10.1103/PhysRevE.94.022144](https://doi.org/10.1103/PhysRevE.94.022144)**I. INTRODUCTION**

Understanding how a system responds to variations of its parameters is one of the basic features of science. It is well known that systems in thermodynamic equilibrium when slightly perturbed find their way back to a new steady regime by dissipation. The spontaneous correlations in the unperturbed system between this transient entropic change and an observable anticipates how that observable would react to the actual perturbation. This is at the basis of the fluctuation-dissipation theorem and of related response relations, which hold in great generality in equilibrium [1,2].

Out of equilibrium, in contrast, there are multiple linear response theories [2–4], some based on the manipulation of the density of states [5–9], some on dynamical system techniques for evolving observables [10–12], and some on a path-weight approach for stochastic systems [13–17]. The latter has revealed that entropy production is not sufficient for understanding the linear response of nonequilibrium systems.

Within the linear response theory one finds recent approaches focusing on temperature perturbations [18–26], which lead for instance to a formulation of nonequilibrium heat capacity [19], a notion that should be useful for constructing a steady-state thermodynamics [27–31]. The question is how a system far from equilibrium reacts to a change of one or many of its bath temperatures. For example, one could be interested in the response to temperature variations of a glassy system undergoing a relaxation process [32,33]. Alternatively, a nonequilibrium steady state may be imposed by putting the system in contact with two reservoirs at different temperatures [34–36]. This is the case of an experiment recently realized with a simple desktop electric circuit in which one resistor was kept at room temperature while the other was maintained at a lower temperature [34,35].

In this paper, we analyze the experiments of the thermally unbalanced electric circuit [34,35]. The primary goal of this work is to show how to apply in practice a fluctuation-response relation [25,26] for computing the susceptibility of the system to a change of one temperature. This is a stand-alone procedure for predicting the thermal linear response of the system. Just to validate its results, we compare them with an alternative estimate of the susceptibility, which is introduced here to exploit the knowledge of the steady-state data (which are accessible for the simple system analyzed), used by us in a reweighted form to replace the actual application of the perturbation. This useful procedure constitutes a new result of this work. We also show the connection of this reweighting procedure with another fluctuation-response relation based on the steady-state distribution, as put forward by Seifert and Speck [8].

In the following section we describe the experimental setup, then we recall the structure of the fluctuation-response relation and we specialize it to our system. In Sec. IV we introduce the reweighting procedure, and in Sec. V we show how to compute a nonequilibrium version of the heat capacity. The conclusions are followed by an appendix in which we recall in detail the steps to compute the Gaussian steady-state distribution of linear stable systems and we specify its form for the electrical circuit.

II. EXPERIMENTAL SETUP

Our experimental setup is sketched in Fig. 1(a). It is constituted by two resistors R_1 and R_2 , which are kept at different temperatures T_1 and T_2 , respectively. These temperatures are controlled by thermal baths, and T_2 is kept fixed at 296 K whereas T_1 can be set at a value between 296 and 88 K by using the stratified vapor above a liquid nitrogen bath. The coupling capacitor C controls the electrical power exchanged between the resistors and, as a consequence, the energy exchanged between the two baths. No other coupling exists between the two resistors, which are inside two separated screened boxes. The quantities C_1 and C_2 are the capacitances of the circuits

*baiesi@pd.infn.it

†yolcu@pd.infn.it

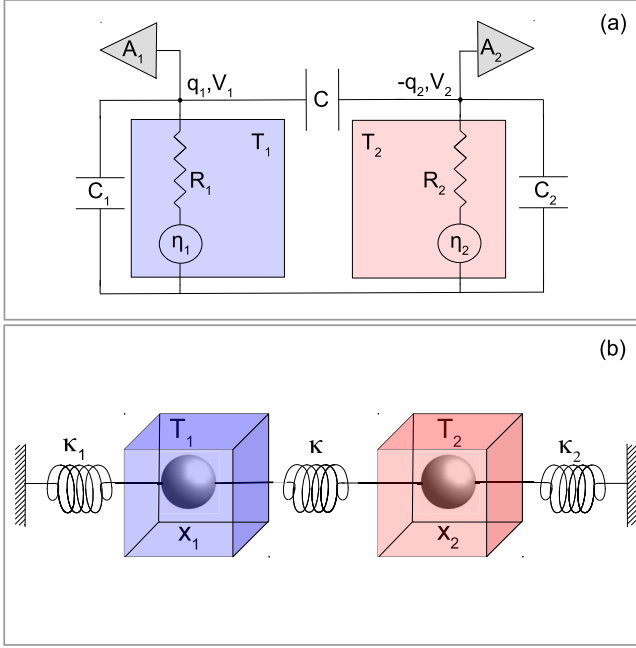


FIG. 1. (a) Diagram of the circuit. The resistor R_1 is kept at temperature T_1 while R_2 is always at room temperature $T_2 = 296$ K. They are coupled via the capacitor C . The capacitors C_1 and C_2 account for the capacitance of the wiring, etc. The voltage generators η_1 and η_2 represent thermal fluctuations of the voltage that the resistors undergo. (b) Equivalent mechanical system with two Brownian particles moving in fluids at different temperatures T_1 and T_2 , but trapped and coupled by harmonic springs.

and the cables. Two extremely-low-noise amplifiers A_1 and A_2 [37] measure the voltage V_1 and V_2 across the resistors R_1 and R_2 , respectively. All the relevant quantities considered in this paper can be derived by the measurements of V_1 and V_2 , as discussed below. In particular, the relationships between the measured voltages and the charges are

$$q_1 = (V_1 - V_2)C + V_1 C_1, \quad (1)$$

$$q_2 = (V_1 - V_2)C - V_2 C_2. \quad (2)$$

Assuming an initially neutral circuit, we denote by q_1 the charge that has flown through the resistor R_1 into the node at potential V_1 , and by q_2 the charge that has flown through R_2 out of the node at V_2 . By analyzing the circuit one finds that the equations of motion for these charges are

$$R_1 \dot{q}_1 = -\frac{C_2}{X} q_1 + \frac{C}{X} (q_2 - q_1) + \eta_1, \quad (3a)$$

$$R_2 \dot{q}_2 = -\frac{C_1}{X} q_2 + \frac{C}{X} (q_1 - q_2) + \eta_2, \quad (3b)$$

where

$$X = CC_1 + CC_2 + C_1 C_2, \quad (4)$$

and $\eta_i(t)$ is white noise satisfying $\langle \eta_i(t) \eta_j(t') \rangle = 2\delta_{ij} k_B T_i R_i \delta(t - t')$. Indeed, in Fig. 1(a) the two resistances have been drawn with their associated thermal noise generators

TABLE I. Mapping between electrical quantities and mechanical quantities. Note the inversion of indices for $C_2/X \rightarrow \kappa_1$ and $C_1/X \rightarrow \kappa_2$.

Electrical	Mechanical
q_1	x_1
q_2	x_2
$1/R_1$	μ_1 (mobility)
$1/R_2$	μ_2
C_2/X	κ_1 (spring constant)
C_1/X	κ_2
C/X	κ

η_1 and η_2 , whose power spectral densities are given by the Nyquist formula $|\tilde{\eta}_m|^2 = 4k_B R_m T_m$, with $m = 1, 2$.

More details on the experimental setup can be found in Refs. [34,35]. For the data used for the analysis discussed in the following section, the values of the components are $C = 100$ pF, $C_1 = 680$ pF, $C_2 = 420$ pF, and $R_1 = R_2 = 10$ M Ω . The longest characteristic time of the system is $Y = (C_1 + C)R_1 + (C_2 + C)R_2$, which for the mentioned parameter values is $Y = 13$ ms.

III. THERMAL RESPONSE

The system has $N = 2$ degrees of freedom. Equations (3) can be mapped onto the mechanical system in Fig. 1(b) involving two Brownian particles coupled by harmonic springs,

$$\dot{x}_1 = \mu_1 F_1(\mathbf{x}) + \sqrt{2\mu_1 k_B T_1} \xi_1, \quad (5a)$$

$$\dot{x}_2 = \mu_2 F_2(\mathbf{x}) + \sqrt{2\mu_2 k_B T_2} \xi_2. \quad (5b)$$

Here, $\mathbf{x} = (x_1, x_2)$ are the two positions with $x_i = 0$ when the springs are at rest, $\mathbf{T} = (T_1, T_2)$ the temperatures, and the (harmonic) forces $\mathbf{F} = (F_1, F_2)$ are derived from the potential

$$U(\mathbf{x}) = \frac{1}{2} [\kappa_1 x_1^2 + \kappa (x_2 - x_1)^2 + \kappa_2 x_2^2]. \quad (6)$$

The detailed mapping between the electrical and mechanical models is summarized in Table I; for instance, the admittance $1/R_1$ is mapped to the mobility μ_1 . Again, each Gaussian white noise ξ_j is uncorrelated from the other,

$$\langle \xi_j(t) \xi_{j'}(t') \rangle = \delta(t - t') \delta_{jj'}. \quad (7)$$

This recasting in the form (5) allows us to use some recently introduced thermal response formulas [25,26]. They predict the linear response of an overdamped stochastic system with additive noise, in general nonequilibrium conditions, when the perturbation is a change of one or more temperatures. In accordance with the presentation of that approach, we choose natural units ($k_B = 1$) in the following, taking temperatures to have dimensions of energy.

The thermal susceptibility of a state observable $\mathcal{O}(\mathbf{x})$ is defined as the response to a step variation $\mathbf{T} \rightarrow \Theta$ of the set of temperatures, parametrized by a function $\theta(t) = 0$ for times $t < 0$ and $\theta(t) = \theta$ constant for $t \geq 0$. In particular, with indicators ϵ_i ($1 \leq i \leq N$) that specify which temperatures

receive the perturbation, here we write

$$\Theta \equiv (T_1 + \epsilon_1 \theta, T_2 + \epsilon_2 \theta). \quad (8)$$

The susceptibility as a function of time t is then

$$\chi_{\mathcal{O}}^\theta(t) = \lim_{\theta \rightarrow 0} \frac{\langle \mathcal{O}(\mathbf{x}(t)) \rangle_{T, \Theta} - \langle \mathcal{O}(\mathbf{x}(t)) \rangle_{T, T}}{\theta}. \quad (9)$$

In the averages $\langle \dots \rangle_{T, T'}$, the first subscript T represents the initial ($t < 0$) temperatures, while the second subscript T' represents the temperatures under which the observed dynamics ($t \geq 0$) takes place.

A recent fluctuation-response relation [25,26] expresses the susceptibility (9) of the state observable $\mathcal{O}(\mathbf{x})$ as a sum,

$$\chi_{\mathcal{O}}(t) = S_1 + S_2 + K_1 + K_2, \quad (10)$$

where the terms are

$$S_1 = - \left\langle \mathcal{O}(t) \sum_i \frac{\epsilon_i}{2T_i^2} \int_0^t \dot{x}_i(t') F_i(t') dt' \right\rangle, \quad (11a)$$

$$S_2 = \left\langle \mathcal{O}(t) \sum_i \frac{\epsilon_i}{4T_i^2} \sum_{j=1}^N \left(\frac{T_i}{T_j} - 1 \right) \int_0^t [x_i \dot{x}_j \partial_j F_i](t') dt' \right\rangle, \quad (11b)$$

$$K_1 = \left\langle \mathcal{O}(t) \sum_i \frac{\epsilon_i}{4T_i^2} \int_0^t [\mu_i F_i^2 + x_i \mathbb{L}^{(T_i)} F_i](t') dt' \right\rangle, \quad (11c)$$

$$K_2 = \frac{d}{dt'} \left\langle \mathcal{O}(t) \sum_i \frac{\epsilon_i}{8\mu_i T_i^2} x_i^2(t') \right\rangle \Big|_{t'=0}^{t'=t}, \quad (11d)$$

with the shorthand $\partial_j = \partial / \partial x_j$, and $\langle \dots \rangle = \langle \dots \rangle_{T, T}$ denoting unperturbed averages which have an understood dependence on the distribution $\rho_0(\mathbf{x}(0))$ at the time when the perturbation is turned on. (Let us stress that the labels 1,2 of these S and K terms have nothing to do with the index of the resistors, particles, etc.) Integrals are in the Stratonovich sense, hence in their discretized version one performs midpoint averages, such as $\dot{x}(t)F(t)dt \rightarrow [x(t+dt) - x(t)]_{\frac{1}{2}}[F(t+dt) + F(t)]$. (However, temperatures and mobilities do not depend on the coordinates and the interpretation of the stochastic equation is free.)

The term S_1 is a standard correlation between observable and entropy production, but it contains a prefactor $1/2$ not present in the equilibrium version (Kubo formula). The term S_2 instead correlates the observable with another form of entropy production and clearly it is relevant only if $T_j \neq T_i$ for some (i, j) . The terms K_1 and K_2 , previously called the *frenetic* terms [3,20,24–26], instead correlate the observable with time-symmetric aspects of the dynamics. These are necessarily nondissipative in nature. In all cases it is understood that we are dealing with quantities in excess due to the perturbation. The generalized generator

$$\mathbb{L}^{(T_i)} = \sum_j \frac{T_i}{T_j} [\mu_j F_j(\mathbf{x}) \partial_j + \mu_j T_j \partial_j^2] \quad (12)$$

was introduced to describe the evolution of the degrees of freedom in terms of the j th *thermal time* as dictated by the i th

temperature (see Ref. [26] for more details). It differs from the backward generator of the dynamics (5),

$$\mathbb{L} = \sum_{j=1}^N [\mu_j F_j(\mathbf{x}) \partial_j + \mu_j T_j \partial_j^2], \quad (13)$$

whose action on a state function inside an average is expressed as $\frac{d}{dt} \langle \mathcal{O}(\mathbf{x}(t)) \rangle = \langle \mathbb{L} \mathcal{O}(\mathbf{x}(t)) \rangle$. The definition of a thermal time permits us to recast Eq. (5) as isothermal dynamics. For example, if $i = 1$ and hence T_1 is taken as a reference, then the thermal time $\tau_2 = tT_2/T_1$ yields for x_2

$$\frac{dx_2}{d\tau_2} = \frac{T_1}{T_2} \mu_2 F_2(\mathbf{x}) + \sqrt{2\mu_2 k_B T_1} \xi_2(\tau_2), \quad (14)$$

where the different intensity of the noise ξ_2 (it has now T_1 in the prefactor) is associated with a rescaling $\sim T_1/T_2$ of the mechanical force F_2 .

In our analysis we work with experimental trajectory data collected in steady states, where $\frac{d}{dt'} \langle \mathcal{O}(t)x^2(t') \rangle = -\frac{d}{dt'} \langle \mathcal{O}(t)x^2(t') \rangle = -\langle \mathbb{L} \mathcal{O}(t)x^2(t') \rangle$ for $t \geq t'$. Hence we rather use the alternative form

$$K_2^s = \left\langle \mathbb{L} \mathcal{O}(t) \sum_i \frac{\epsilon_i}{8\mu_i T_i^2} [x_i^2(0) - x_i^2(t)] \right\rangle, \quad (15)$$

because it is numerically more stable than K_2 [26]. Since in the given experimental setup it is natural to manipulate T_1 (while the room temperature T_2 remains unperturbed), we show examples with $\epsilon_1 = 1$ and $\epsilon_2 = 0$. This leads to the susceptibility $\chi_{\mathcal{O}}(t)$ being composed of the specific terms

$$S_1 = -\frac{1}{2T_1^2} \left\langle \mathcal{O}(t) \int_0^t \dot{x}_1(t') F_1(t') dt' \right\rangle, \quad (16a)$$

$$S_2 = \frac{1}{4T_1^2} \left\langle \mathcal{O}(t) \left(\frac{T_1}{T_2} - 1 \right) \int_0^t [x_1 \dot{x}_2 \partial_2 F_1](t') dt' \right\rangle, \quad (16b)$$

$$K_1 = \frac{1}{4T_1^2} \left\langle \mathcal{O}(t) \int_0^t [\mu_1 F_1^2 + x_1 \mathbb{L}^{(T_1)} F_1](t') dt' \right\rangle, \quad (16c)$$

$$K_2 = \frac{1}{8\mu_1 T_1^2} \langle \mathbb{L} \mathcal{O}(t) [x_1^2(0) - x_1^2(t)] \rangle, \quad (16d)$$

with $\mathbb{L}^{(T_1)} = \mu_1 [F_1 \partial_1 + T_1 \partial_1^2] + \mu_2 [\frac{T_1}{T_2} F_2 \partial_2 + T_1 \partial_2^2]$. Note that we have dropped the superscript “s” from K_2 .

The susceptibility is found as the sum of these correlations with fluctuating trajectory functionals, *predicting* the susceptibility without actually performing perturbations. Before showing examples, in the next section we describe a second procedure aimed at computing the response in a more *direct* way. The latter will then be compared with the fluctuation-response results above.

IV. REWEIGHTING

In the analysis via the fluctuation-response relation exposed in the previous section, we deal with experimental data collected in steady states at various temperatures $T = (T_1, T_2)$. Next we show that the same data can be used to extract a

form of the susceptibility that is equivalent to Eq. (9). This means that we can bypass once again the step of the actual perturbation of the system in the laboratory.

In the definition (9) what is not useful is that one average is over trajectories under the perturbed Θ , while the other is over unperturbed trajectories. In steady-state experiments, trajectories of the former kind are not available. To sidestep this, we find it convenient to consider the alternative formula¹

$$\chi_{\mathcal{O}}^{\theta}(t) = \lim_{\theta \rightarrow 0} \frac{\langle \mathcal{O}(\mathbf{x}(t)) \rangle_{\Theta, T} - \langle \mathcal{O}(\mathbf{x}(t)) \rangle_{\Theta, \Theta}}{-\theta}, \quad (17)$$

because with this form, we can reexpress both averages above in terms of steady-state averages at T by the following arguments.

First, take the steady-state average

$$\begin{aligned} \langle \mathcal{O}(\mathbf{x}(t)) \rangle_{\Theta, \Theta} &= \langle \mathcal{O}(\mathbf{x}) \rangle_{\Theta, \Theta} = \int d\mathbf{x} \rho_{\Theta}(\mathbf{x}) \mathcal{O}(\mathbf{x}) \quad (18) \\ &= \int d\mathbf{x} \rho_T(\mathbf{x}) \frac{\rho_{\Theta}(\mathbf{x})}{\rho_T(\mathbf{x})} \mathcal{O}(\mathbf{x}) \\ &= \left\langle \frac{\rho_{\Theta}(\mathbf{x})}{\rho_T(\mathbf{x})} \mathcal{O}(\mathbf{x}) \right\rangle_{T, T}. \end{aligned} \quad (19)$$

Second, by denoting the probability measure of path $[\mathbf{x}]$ under temperatures T by $\mathcal{D}\mathbf{x} P_T[\mathbf{x}]$ [where $P_T[\mathbf{x}]$ is the path weight, given that it starts from $\mathbf{x}(0)$], take the transient average

$$\begin{aligned} \langle \mathcal{O}(\mathbf{x}(t)) \rangle_{\Theta, T} &= \int \mathcal{D}\mathbf{x} P_T[\mathbf{x}] \rho_{\Theta}(\mathbf{x}(0)) \mathcal{O}(\mathbf{x}(t)) \quad (20) \\ &= \int \mathcal{D}\mathbf{x} P_T[\mathbf{x}] \rho_T(\mathbf{x}(0)) \frac{\rho_{\Theta}(\mathbf{x}(0))}{\rho_T(\mathbf{x}(0))} \mathcal{O}(\mathbf{x}(t)) \quad (21) \\ &= \left\langle \frac{\rho_{\Theta}(\mathbf{x}(0))}{\rho_T(\mathbf{x}(0))} \mathcal{O}(\mathbf{x}(t)) \right\rangle_{T, T}. \end{aligned} \quad (22)$$

Thus, by this reweighting via stationary distributions, both averages appearing in Eq. (17) have been reformulated as steady-state averages at T , and the susceptibility becomes

$$\begin{aligned} \chi_{\mathcal{O}}^{\theta}(t) &= \lim_{\theta \rightarrow 0} \frac{-1}{\theta} \left(\left\langle \frac{\rho_{\Theta}(\mathbf{x}(0))}{\rho_T(\mathbf{x}(0))} \mathcal{O}(\mathbf{x}(t)) \right\rangle_{T, T} \right. \\ &\quad \left. - \left\langle \frac{\rho_{\Theta}(\mathbf{x})}{\rho_T(\mathbf{x})} \mathcal{O}(\mathbf{x}) \right\rangle_{T, T} \right). \end{aligned} \quad (23)$$

The second single-time average can be written at any instant of time due to time-translation invariance. As such, substituting the particular points $\mathbf{x}(0)$ or $\mathbf{x}(t)$, one obtains, respectively,

$$\chi_{\mathcal{O}}^{\theta}(t) = \lim_{\theta \rightarrow 0} \frac{-1}{\theta} \left\langle [\mathcal{O}(\mathbf{x}(t)) - \mathcal{O}(\mathbf{x}(0))] \frac{\rho_{\Theta}(\mathbf{x}(0))}{\rho_T(\mathbf{x}(0))} \right\rangle, \quad (24)$$

or

$$\chi_{\mathcal{O}}^{\theta}(t) = \lim_{\theta \rightarrow 0} \frac{1}{\theta} \left\langle \mathcal{O}(\mathbf{x}(t)) \left[\frac{\rho_{\Theta}(\mathbf{x}(t))}{\rho_T(\mathbf{x}(t))} - \frac{\rho_{\Theta}(\mathbf{x}(0))}{\rho_T(\mathbf{x}(0))} \right] \right\rangle. \quad (25)$$

Again, $\langle \dots \rangle$ means the steady state average $\langle \dots \rangle_{T, T}$ with the available data. Both formulas can be used to extract the

¹Equation (17) is a rewriting of Eq. (9) with T and Θ interchanged, which is equivalent to Eq. (9) when the limit of $T \rightarrow \Theta$ (i.e., $\theta \rightarrow 0$) is taken.

response of the system to a step change of temperature(s) performed at $t = 0$. In our analysis we chose to use Eq. (24).

It is interesting to connect these expressions with previous response relations based on the knowledge of the steady-state distribution. One notes that, in the limit $\theta \rightarrow 0$, the reweighting factor

$$\frac{\rho_{\Theta}}{\rho_T} \simeq \frac{\rho_T + \theta \partial_{\theta} \rho_{\Theta}}{\rho_T} = 1 + \theta \partial_{\theta} \ln \rho_{\Theta}. \quad (26)$$

Substituting this limit, and dropping for simplicity the temperature indices, the second expression (25) for susceptibility above becomes

$$\chi_{\mathcal{O}}(t) = \langle \mathcal{O}(\mathbf{x}(t)) [\partial_{\theta} \ln \rho(\mathbf{x}(t)) - \partial_{\theta} \ln \rho(\mathbf{x}(0))] \rangle, \quad (27)$$

implying that it comes from a response function [$\chi_{\mathcal{O}}(t) = \int_0^t ds R_{\mathcal{O}}(t-s)$]

$$R(t-s) = \frac{d}{ds} \langle \mathcal{O}(\mathbf{x}(t)) \partial_{\theta} \ln \rho(\mathbf{x}(s)) \rangle. \quad (28)$$

Equivalently, defining the stochastic entropy $\mathcal{I} = -\ln \rho$,

$$R(t-s) = -\frac{d}{ds} \langle \mathcal{O}(\mathbf{x}(t)) \partial_{\theta} \mathcal{I}(\mathbf{x}(s)) \rangle, \quad (29)$$

which is Seifert and Speck's response formula [8] for steady states, with the only difference being that θ carries a physical dimension while usually the perturbation was expressed in terms of a dimensionless parameter h .

While an analytical expression such as Eq. (29) is more elegant than Eqs. (24) or (25), on the practical side the former may be less convenient. First of all, an analytical expression for the stationary distribution may not be known or calculable, in which case it must be actually measured at two different temperatures and the θ derivative will have to be performed discretely, which is equivalent to using the expressions prior to Eq. (26). Second, even if an analytical expression for the stationary distribution is available (as it is for the present system of interest; see details in the appendix), its θ derivative might be too unwieldy to work with, from an implementation point of view. A discrete approximation for the derivative, such as Eq. (24), is simpler to handle. We have indeed followed this path, by using analytical expressions for the distributions ρ_{Θ} and ρ_T , choosing $\Theta = (T_1 + \theta, T_2)$ with $\theta = T_1/100$.

V. NONEQUILIBRIUM HEAT CAPACITY

In this section we show the analysis of experimental data, which show that the fluctuation-response relation $\chi_{\mathcal{O}}(t) = S_1 + S_2 + K_1 + K_2$ with terms listed in Eq. (16) can reliably compute the susceptibility of the system. The knowledge of the steady-state distribution allows us to use the formula introduced in Eq. (24) and to compute the response independently. The two versions turn out to yield results in good agreement with each other.

The averages used to compute susceptibilities are performed over trajectories that extend over ≈ 50 ms, with time steps of length $\Delta t = 1/8192$ s ≈ 0.122 ms. Each trajectory is extracted by choosing a different starting point from the steady-state sampling. Three cases are considered, one in the equilibrium condition $T_1 = T_2 = 296$ K ($\approx 7 \times 10^7$ trajectories) and two far from equilibrium, $T_1 = 140$ K ($\approx 2.6 \times 10^7$ trajectories) and $T_1 = 88$ K ($\approx 4.6 \times 10^7$ trajectories).

As an observable $\mathcal{O}(\mathbf{x})$ —where we recall that $\mathbf{x} = (x_1, x_2) = (q_1, q_2)$ —we consider the total electrostatic energy (6) of the system, in accord with the mapping of Table I between electrical and mechanical quantities. The backward generator acting on this observable, $\mathbb{L}\mathcal{O}$ appearing in Eq. (16d), becomes

$$\begin{aligned} \mathbb{L}U(\mathbf{x}) = & \kappa_1\mu_1[F_1(\mathbf{x})x_1 + T_1] + \kappa_2\mu_2[F_2(\mathbf{x})x_2 + T_2] \\ & + \kappa\{\mu_1[F_1(\mathbf{x})(x_1 - x_2) + T_1] \\ & + \mu_2[F_2(\mathbf{x})(x_2 - x_1) + T_2]\}, \end{aligned} \quad (30)$$

where we recall that $k_B = 1$ and temperatures have dimensions of energy. The response of the energy to a change of temperature becomes the nonequilibrium version of the heat capacity if $T_1 \neq T_2$ (a different definition of heat capacity for nonequilibrium systems can be found in Ref. [19]). The following analysis confirms that, in general, this heat capacity cannot be computed only from the correlation between energy and heat flowing into the system [19,20,24–26], unless this is in equilibrium.

The susceptibility χ_U of the internal energy to a change of T_1 is shown in Fig. 2 as a function of time for the three values of T_1 . It correctly converges to a constant value for large times, although its single terms may be extensive in time in nonequilibrium conditions. We have also an analytical argument predicting that such a constant value should be $1/2$. It is based on recently proposed mesoscopic virial equations [38]. For each degree of freedom i in an overdamped system subject to multiple reservoirs, we have

$$-\langle x_i F_i(\mathbf{x}) \rangle = T_i. \quad (31)$$

In our system with quadratic potential energy this implies $\langle U(\mathbf{x}) \rangle = T_1/2 + T_2/2$ in a steady state. Therefore, it is expected that the susceptibility $\chi_U(t) = \partial\langle U \rangle / \partial T_1 \rightarrow 1/2$ as $t \rightarrow \infty$. This is indeed observed in the top panel of Fig. 2, where the steady state is an equilibrium state, with $T_1 = T_2$. The asymptotic value of $1/2$ for the susceptibility is also fairly well reached by the data in the lower panels of Fig. 2; a possible explanation of the slight disagreement is given in the next paragraph. In equilibrium (top panel), K_1 and S_2 vanish while K_2 is equal to S_1 ; that is, the response is given by twice S_1 . This is essentially the Kubo formula, stating that, in equilibrium, the response of an observable is given by its correlations with the entropy produced in the environment (heat flow divided by reservoir temperature), which is confirmed by the form (16a) of S_1 . [The extra factor of $1/T_1$ in Eq. (16) has to do with the units of susceptibility.] On the other hand, out of equilibrium, the equality between S_1 and K_2 is lost in addition to K_1 and S_2 no longer vanishing, as demonstrated by the two bottom panels of Fig. 2: All the terms S_1 , S_2 , K_1 , and K_2 of Eq. (16) composing $\chi_{\mathcal{O}}$ are all relevant. The correlation S_1 between the observable and the heat flow is not sufficient anymore in nonequilibrium systems. The frenetic terms K_1 , K_2 and the new entropy production term S_2 are also relevant for predicting the nonequilibrium response.

While the susceptibility at equilibrium ($T_1 = T_2$) attains the expected asymptotic value of $1/2$ fairly closely, the susceptibility out of equilibrium ($T_1 \neq T_2$) seems to fall a bit short. We argue that this has to do with the inevitable limitation

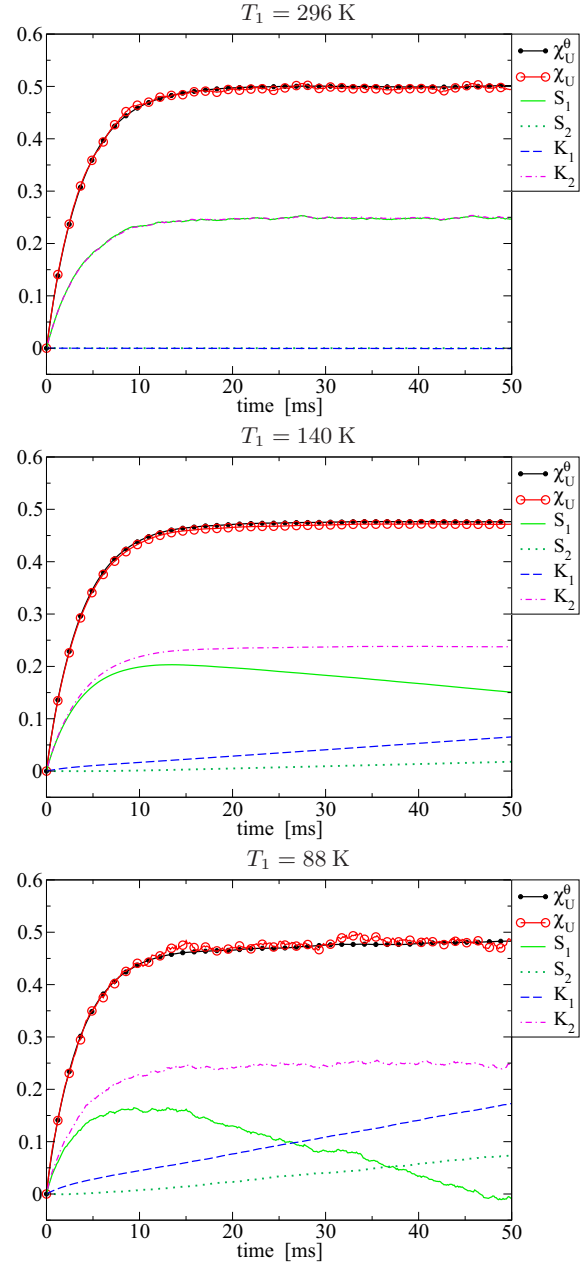


FIG. 2. Response of the total energy U to a change of T_1 , for equilibrium ($T_1 = 296 \text{ K} = T_2$) and for nonequilibrium ($T_1 = 140 \text{ K}$ and $T_1 = 88 \text{ K}$). The susceptibility χ_U computed with the fluctuation-response relation (10) and its terms S_1 , S_2 , K_1 , K_2 are shown. The susceptibility χ_U^θ computed with the reweighting formula (24) agrees with χ_U .

on the time resolution of the trajectory measurements, since numerical simulations of an equivalent system also exhibit the same feature when the time discretization becomes coarse. Indeed, the sampling interval in the experiments ($\approx 0.1 \text{ ms}$) is not *much* smaller than the dynamical timescale $Y = 13 \text{ ms}$ in the circuit, which one can confirm visually from the plots in Fig. 2. The reason why it is the nonequilibrium susceptibilities which suffered more from this quantization error is likely as follows: Out of equilibrium, trajectory functionals like

entropy production are numerically larger than in equilibrium, amplifying any error in the trajectory.

In all examples we also plot the susceptibility χ_U^θ computed with Eq. (24). Clearly there is a very good agreement between this estimate and χ_U for all times, including the deviation from the asymptotic value 1/2 for large times. This suggests that both approaches work well and corroborates our explanation of the slight offset in the asymptotic value, as also χ_U^θ should be affected by the time-step discretization.

VI. CONCLUSION

We have shown that experimental steady-state data can be used to predict the thermal linear response of an electric circuit, even if it works in a thermally unbalanced nonequilibrium regime due to a cryogenic bath applied to one of the two resistors. We have used a recent nonequilibrium response relation for our analysis. This approach requires the knowledge of the forces acting on each degree of freedom, an information easily available in our case. The nonequilibrium version of the heat capacity provides a simple demonstration of the fact that, in general, one cannot expect to predict the response of the energy to thermal variations just from the unperturbed correlations between energy and fluctuating heat flows, as one would do by using the standard fluctuation-dissipation theorem for equilibrium systems. Also, nondissipative aspects play a crucial role: The response includes correlations between the observable and the so-called frenesy of the system [3,4], which is a measure of how frantically the system wanders about in phase space. Our example of generalized heat capacity, in terms of the response of the total energy of the system, is relevant in the context of steady-state thermodynamics [27–31]. Other definitions of heat capacity are possible; for example, in terms of excess heat flow with respect to the housekeeping heat flow [19].

To have a comparison with an independent method for computing the susceptibility, we also introduced a reweighting procedure that has the advantage of needing no more than the same steady-state data. The second method estimates the susceptibility of the system in a more direct sense; namely, mimicking actual finite perturbations of the system. This procedure is simple to implement and is related to a linear response formula also based on the knowledge of the steady-state distribution.

APPENDIX: GAUSSIAN STEADY-STATE DISTRIBUTIONS

We review the procedure used to obtain the steady-state distribution for linear overdamped stochastic systems with additive noise.

Consider a process given by the stochastic differential equation

$$\dot{\mathbf{x}} = -\mathbf{A}\mathbf{x} + \sqrt{2D}\boldsymbol{\xi}, \quad (\text{A1})$$

with $\boldsymbol{\xi}$ being N -dimensional uncorrelated noise and \mathbf{x} being the N -dimensional state. Here, \mathbf{A} and D are $N \times N$ positive-definite constant matrices. The ensemble current corresponding to these degrees of freedom follows as

$$\mathbf{J} = -\rho\mathbf{A}\mathbf{x} - D\nabla\rho, \quad (\text{A2})$$

with the Fokker–Planck equation $\partial_t\rho + \nabla \cdot \mathbf{J} = 0$. Thus, stationarity implies (index notation hereafter)

$$0 = -\partial_i J_i \quad (\text{A3})$$

$$= \partial_i(\rho A_{ij}x_j) + D_{ij}\partial_i\partial_j\rho \quad (\text{A4})$$

$$= \rho A_{ii} + A_{ij}x_j\partial_i\rho + D_{ij}\partial_i\partial_j\rho. \quad (\text{A5})$$

Clearly, an exponential quadratic form would satisfy this equation and the ansatz

$$\rho(\mathbf{x}) = \sqrt{\frac{\det G}{(2\pi)^N}} e^{-\frac{1}{2}x_i G_{ij}x_j}, \quad (\text{A6})$$

with G positive definite, yields

$$0 = A_{ii} - A_{ij}x_j G_{ik}x_k + D_{ij}(G_{ik}x_k G_{jl}x_l - G_{ij}) \quad (\text{A7})$$

$$= A_{ii} - D_{ij}G_{ij} - x_kx_l(A_{il}G_{ik} - G_{ik}D_{ij}G_{jl}). \quad (\text{A8})$$

By using the symmetry of G_{ij} and matrix notation, this can be rewritten as

$$\text{Tr}(\mathbf{A} - D\mathbf{G}) = \mathbf{x}^\dagger(\mathbf{G}\mathbf{A} - \mathbf{G}D\mathbf{G})\mathbf{x}. \quad (\text{A9})$$

Since this is supposed to hold for any \mathbf{x} , both sides must vanish. For the right-hand side, this implies that the matrix $\mathbf{G}\mathbf{A} - \mathbf{G}D\mathbf{G}$ is skew symmetric, which means that it has vanishing symmetric part,

$$\mathbf{G}\mathbf{A} + \mathbf{A}^\dagger\mathbf{G} = 2\mathbf{G}D\mathbf{G}, \quad (\text{A10})$$

or, equivalently,

$$\mathbf{A}\mathbf{G}^{-1} + \mathbf{G}^{-1}\mathbf{A}^\dagger = 2D. \quad (\text{A11})$$

The left-hand side of Eq. (A9) also vanishes, as required, when a G_{ij} satisfying Eq. (A11) is found.

Being a linear equation in the unknown entries of G^{-1} , one can imagine rewriting Eq. (A11) so as to treat those unknowns as a vector (likewise the right-hand side), and afterwards inverting the matrix equation. This is achieved by resorting to the Kronecker product, denoted by \otimes , and a “vectorization” operation, denoted as “vec,” which amounts to stacking the columns of a matrix into a single column. Equation (A11) is recast in the form

$$(\mathbf{I} \otimes \mathbf{A} + \mathbf{A} \otimes \mathbf{I}) \text{vec } \mathbf{G}^{-1} = 2 \text{vec } D. \quad (\text{A12})$$

Hence we find G^{-1} via

$$\text{vec } \mathbf{G}^{-1} = 2(\mathbf{I} \otimes \mathbf{A} + \mathbf{A} \otimes \mathbf{I})^{-1} \text{vec } D \quad (\text{A13})$$

followed by an “un-vec,” i.e., a procedure reverting back from vectorized matrices to actual ones.

Circuit experiments

In the electric circuit experiments, the equation of motion for the charges is of the form

$$\dot{\mathbf{q}} = -\mathbf{R}^{-1}\mathbf{C}^{-1}\mathbf{q} + \mathbf{R}^{-1}\sqrt{2RT}\boldsymbol{\xi}, \quad (\text{A14})$$

where

$$\mathcal{C} = \begin{bmatrix} C + C_1 & C \\ C & C + C_2 \end{bmatrix}, \quad (\text{A15})$$

$$\mathcal{C}^{-1} = \frac{1}{X} \begin{bmatrix} C + C_2 & -C \\ -C & C + C_1 \end{bmatrix}, \quad (\text{A16})$$

$$R = \begin{bmatrix} R_1 & 0 \\ 0 & R_2 \end{bmatrix}, \quad (\text{A17})$$

$$T = \begin{bmatrix} T_1 & 0 \\ 0 & T_2 \end{bmatrix} \quad (\text{A18})$$

[$X = \det \mathcal{C}$ was defined in Eq. (4)]. Thus, we identify $A = R^{-1}\mathcal{C}^{-1}$ and $D = R^{-1}T$. Through Eq. (A13) and inverting the resulting matrix G , we have

$$G = \frac{Y}{Z} \begin{bmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{bmatrix}, \quad (\text{A19})$$

with

$$Y = R_1 R_2 (\det \mathcal{C}) (\text{Tr } A) \\ = (C + C_1)R_1 + (C + C_2)R_2, \quad (\text{A20})$$

$$Z = X[Y^2 T_1 T_2 + R_1 R_2 C^2 (T_1 - T_2)^2], \quad (\text{A21})$$

and

$$g_{11} = T_2 Y (C + C_2) + (T_1 - T_2) R_1 C^2, \quad (\text{A22})$$

$$g_{12} = -(C + C_1) C R_1 T_1 - (C + C_2) C R_2 T_2, \quad (\text{A23})$$

$$g_{21} = g_{12}, \quad (\text{A24})$$

$$g_{22} = T_1 Y (C + C_1) + (T_2 - T_1) R_2 C^2. \quad (\text{A25})$$

We have thus all the elements for computing the steady-state distribution (A6) analytically at any combination of temperatures T_1, T_2 .

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Interacting Brownian dynamics in a nonequilibrium particle bathStefano Steffenoni,^{1,2,*} Klaus Kroy,^{2,†} and Gianmaria Falasco^{2,‡}¹*Max Planck Institute for Mathematics in the Sciences, Inselstrasse 22, 04103 Leipzig, Germany*²*Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, D-04009 Leipzig, Germany*

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We set up a mesoscopic theory for interacting Brownian particles embedded in a nonequilibrium environment, starting from the microscopic interacting many-body theory. Using nonequilibrium linear-response theory, we characterize the effective dynamical interactions on the mesoscopic scale and the statistics of the nonequilibrium environmental noise, arising upon integrating out the fast degrees of freedom. As hallmarks of nonequilibrium, the breakdown of the fluctuation-dissipation and action-reaction relations for Brownian degrees of freedom is exemplified with two prototypical models for the environment, namely active Brownian particles and stirred colloids.

DOI: [10.1103/PhysRevE.94.062139](https://doi.org/10.1103/PhysRevE.94.062139)**I. INTRODUCTION**

The notion of Brownian motion refers to the thermal fluctuations of some mesoscopic particles in contact with a bath of smaller particles. Colloidal beads dissolved in a simple fluid are the historical paradigm. But the concept generalizes to any slow mesoscopic degrees of freedom in contact with a bath of fast microscopic degrees of freedom. In fact, there are wide-ranging applications of the basic theme outside the realm of physics [1]. The essential feature is a scale separation between the Brownian and bath degrees of freedom that allows for some systematic coarse-graining of an otherwise intractable many-body system. A convenient approach to formalize this seminal insight is via (generalized) Langevin equations, which can be formulated for a wide variety of phenomena and have helped to rationalize a range of interesting phenomena from long-time tails [2] to critical fluctuations [3]. They have therefore become a prevalent tool in the quantitative description of soft matter and, more generally, noisy systems.

Even though there exist systematic derivations of such mesoscopic equations of motion from an underlying microscopic many-body Hamiltonian through the elimination of the fast degrees of freedom [4–6], one eventually typically appeals to equilibrium statistical mechanics in order to make the formal expressions practically useful. Namely, to bypass the explicit solution of the microscopic dynamic equations, the “noise” fluctuations that agitate the mesoscopic degrees of freedom are assigned a weight in accordance with Boltzmann’s principle [7]. By construction, their correlations then satisfy detailed balance in the form of a fluctuation-dissipation theorem (FDT) [8]. This implies, in particular, that they induce mesoscopic correlations in accordance with equipartition. Moreover, the average mesoscopic dynamics is found to be a gradient flow in a convex free-energy landscape. Being derived by such a (thermodynamic) potential, the mean effective interactions of the Brownian degrees of freedom themselves obey the action-reaction principle. In other words, in equilibrium stochastic

thermodynamics, the symmetries holding on the microscopic level can essentially be lifted up to the mesoscopic scale. The theory remains valid even when some of these mesoscopic degrees of freedom are externally driven out of equilibrium, as long as local detailed balance persists [9,10], i.e., under the assumption that the source of nonequilibrium does not appreciably affect the (many) bath degrees of freedom. For this reason, the concept of a Brownian scale separation, as embodied in the Langevin equation, has played a central role in the development of a framework of stochastic thermodynamics that reaches out to conditions far from equilibrium [11,12] and in the study of nonequilibrium fluctuation and work relations [13].

In contrast, none of the above symmetry properties generally survives on the Brownian scale if the bath itself is driven out of equilibrium. Not only is the detailed balance of the Brownian degrees of freedom then lost, but also equipartition gives way to a more complex energy partition rule [14], stochastic forces are no longer of gradient-type [15], and the action-reaction principle is violated [16]. In soft matter physics, one finds many examples for interacting probes in nonequilibrium baths. One may naturally think of a suspension of colloids immersed in a nonequilibrium solvent, such as a sheared fluid [17]; a granular [18], glassy [19], or active-particle suspension [20]; or even the cytoplasm of a living cell [21]. It would certainly be of great interest to establish a self-contained coarse-grained description for the colloids in such situations. Yet, the usual equilibrium arguments invoked in the construction of a coarse-grained Langevin description are not any more applicable. So the reduced stochastic description (assuming it still exists) must be found by other means, in the worst case by *explicitly* integrating out the dynamics of the nonequilibrium environment. It should go without saying that, for scientifically or technologically interesting systems, this is almost always an impossible task.

There is thus great interest in defining suitable conditions and finding general approximate methods [22,23] that allow for reliable and useful predictions on the Brownian scale, even if the microscopic degrees of freedom of the environment are driven far from equilibrium. Among other things, such methods should enable us to infer the key properties of the nonequilibrium environment from the observed mesoscopic dynamics. Ideally, they should moreover help to unravel the

*stefano.steffenoni@mis.mpg.de

†klaus.kroy@itp.uni-leipzig.de

‡falasco@itp.uni-leipzig.de

formal structure of the coarse graining, such that we can identify the mechanisms underlying the emergent violations of the detailed-balance and action-reaction principles, which are not always straightforwardly discernible on the mesoscopic scale. Finally, this would allow the logical chain of arguments used to infer environmental conditions from Brownian dynamics to be reversed, namely to tailor some desired mesoscopic properties by a fine-tuning of the nonequilibrium driving of the microstatistics of the environment, with some obvious technological implications.

A good candidate for such an approximate method for bypassing the integration of the microscopic dynamics is suggested by the theory of Brownian motion itself. If the “fast” bath degrees of freedom of some Brownian system themselves admit a coarse-grained description by a mesoscopically driven (generalized) Langevin theory routed in its own equilibrium bath, the resulting theory fulfills all of the above requirements. An example for a successful implementation of such a scheme is provided by the theory of nonequilibrium fluctuating hydrodynamics [24], on which theories of Brownian dynamics in nonequilibrium baths can be based [25,26].

In the following, we pursue this idea in a slightly more abstract and fully particle-based framework, i.e., without appealing to a hydrodynamic limit for the environment degrees of freedom. We do assume, instead, that the environment is made up of some sort of particles that evolve according to some driven Markovian stochastic dynamics enjoying local detail balance. In contrast to standard Brownian dynamics, we thus do not require a direct buffering of the probe degrees of freedom by some equilibrium thermal reservoir but only an indirect one, mediated by the nonequilibrium environment (cf. Fig. 1). Technically, we employ nonequilibrium linear-response theory [27–35] to derive a Langevin equation for the interacting probe particles that we assume to be weakly coupled to the interacting many-body system acting as the environment. Following [36,37], we then go beyond a merely static description that would only account for systematic probe interactions induced by the nonequilibrium environment, such as nonequilibrium depletion forces [38,39]. We explicitly

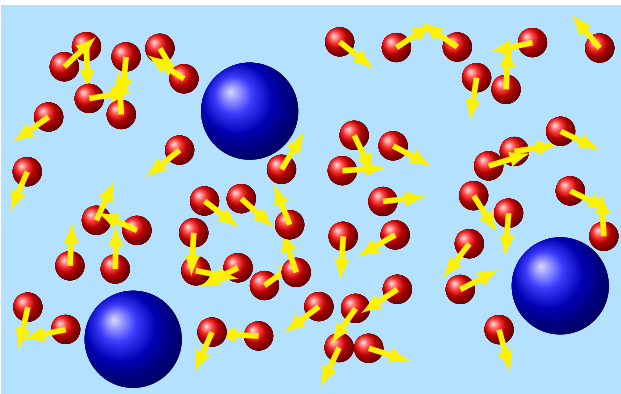


FIG. 1. Schematic representation of the three-level scheme employed by our theory: the probes (blue) representing the system are embedded in a nonequilibrium environment, e.g., a fluid of smaller driven particles (red), which are in contact with a stochastic equilibrium thermal bath (light blue).

look for the fluctuations of such induced forces around their average values. In Sec. II, we obtain formal expressions for these fluctuating forces, the friction, and the noise statistics. When the driving is off, we retrieve the expected detailed balance condition connecting the noise correlation to the friction memory kernel. But we can also analyze how this relation changes when the environment is driven (far) out of equilibrium and quantify the violations of detailed balance and the reciprocal relations in terms of both excess dynamical activity [40–43] and probability currents. The latter result in the lack of an action-reaction principle for the induced probe interactions [16,17,44,45]. Section III exemplifies the theoretical scheme with the help of two paradigmatic examples that can explicitly be worked out. First, we treat analytically a single probe linearly coupled to a fluid of self-propelled particles. This toy model clearly displays the breakdown of detailed balance and allows us to touch on the scope of the notion of effective temperature. Secondly, we employ Brownian dynamics simulations to analyze the effective friction forces induced between two probes suspended in a driven fluid. The numerical evaluation of our general analytic expressions for the time-dependent friction matrix nicely reveals the expected violations of the action-reaction principle, as well as the possible appearance of negative mobility. Finally, in Sec. IV, we conclude with a summary and an outlook.

II. GENERAL THEORY

We consider a d -dimensional system made up of M probe particles, with mass m_i and positions Q_i , which interact with an environment composed of $N \gg 1$ degrees of freedom denoted x_k . The environment is in contact with an equilibrium bath at inverse temperature β . The probes obey Newton’s equation of motion,

$$m_i \ddot{Q}_i = K_i(Q_i) + g_i(\{x_k\}, Q_i), \quad (1)$$

where $g_i \equiv -\lambda \partial_{Q_i} U_i(\{x_k\}, Q_i)$ is the interaction force between the probe i and the environment, with λ a small dimensionless parameter. All the other forces are incorporated in K , which are (optional) direct interactions between the probes and additional external ones. Their specific form is irrelevant in the following. They are only required to be sufficiently confining so as to allow for a unique stationary state. Throughout the text, we use the shorthand $\{ \dots \}_k$ to denote the entire set of degrees of freedom labeled by k . We assume that the environment evolves according to a Markovian stochastic dynamics, enjoying local detail balance. Hence, with respect to standard approaches, we lift such a condition from the dynamics of the system to that of the environment. For concreteness, we can think of the overdamped Langevin equations

$$\dot{x}_k = \mu F - \lambda \mu \sum_{i=1}^M \partial_{x_k} U_i + \sqrt{2\mu/\beta} \xi_k. \quad (2)$$

Here $F(\{x_k\})$ consists of interparticle potential forces $-\partial_{x_k} V(\{x_k\})$, and external ones that may contain a nonpotential driving $f(\{x_k\})$ setting the environment out of equilibrium. The ξ ’s are centered Gaussian noises, white and uncorrelated.

Let $\{Y_i\}$ be the set of average positions around which the probes fluctuate as a consequence of the interactions with the

environment. Here we are concerned with the fluctuations induced by the presence of the environment, for which we seek a reduced description. Namely, we aim at integrating out of (1) the environment coordinates by averaging the probe-environment coupling with the appropriate distribution for x_k . We expect noise and friction in this process, together with indirect forces between the probes, mediated by the environment. Toward that end, we rewrite Eq. (1) as

$$m_i \ddot{Q}_i = K_i + \langle g_i \rangle + \eta_i, \quad (3)$$

where we split the environment-probe coupling into a systematic part $\langle g_i \rangle$ and a random contribution $\eta_i \equiv g_i - \langle g_i \rangle$. The former is defined as the mean force exerted by the environment on probe i , and it reads

$$\langle g_i(\{x_k\}, Q_i) \rangle \equiv \int d\{x_k\} g_i(\{x_k\}, Q_i) \rho(\{x_k\} | \{Q_i\}), \quad (4)$$

with $\rho(\{x_k\} | \{Q_i\})$ the probability density of the environment conditioned by the probes being in positions $\{Q_i\}$. We work under the usual assumptions made in the derivation of Langevin equations, i.e., a small variation of the probe momentum after a single particle-probe interaction (large mass difference), and a weak coupling between probes and environment. Under these conditions, the fluctuations of probe i around the preferred state Y_i are small, and its force on the whole environment can be expanded to linear order in the displacement from Y_i :

$$\lambda \sum_{k=1}^N \partial_{x_k} U_i = \lambda \sum_{k=1}^N \partial_{x_k} U_i \Big|_{Q_i=Y_i} - [Q_i(t) - Y_i] \sum_{k=1}^N \partial_{x_k} g_i \Big|_{Q_i=Y_i}. \quad (5)$$

Here it is useful to regard g_i as an external potential perturbing the environment, modulated in time via the protocol $Q_i(t) - Y_i$. In view of (5), it is then natural to express the conditional average (4) in terms of unperturbed averages $\langle \dots \rangle^0$, corresponding to all probes sitting in the mean positions $\{Y_i\}$. To do so, we make use of the response theory for perturbations about nonequilibrium states. The linear-response formula in general reads [46]

$$\langle \mathcal{A}(t) \rangle = \langle \mathcal{A}(t) \rangle^0 + \frac{\beta}{2} \sum_j \int_{t_0}^t ds h_j(s) \times \left(\frac{d}{ds} \langle \mathcal{B}_j(s); \mathcal{A}(t) \rangle^0 - \langle L \mathcal{B}_j(s); \mathcal{A}(t) \rangle^0 \right), \quad (6)$$

where \mathcal{A} is the observable of interest, and \mathcal{B}_j are the perturbation potentials switched on at time t_0 and modulated in time through the protocol $h_j(s)$. The operator L and the average $\langle \dots; \dots \rangle^0$ stand for, respectively, the backward generator of the unperturbed dynamics and the connected average with respect to it. In (6) the first integrand is the usual correlation of the observable with the entropy production, as appears in the Kubo formula. The second one is a frenetic contribution that contains the excess dynamical activity, $L \mathcal{B}_j$, caused by the perturbation. In equilibrium, they make equal

contributions [34]:

$$\frac{d}{ds} \langle \mathcal{B}_j(s); \mathcal{A}_i(t) \rangle^{\text{eq}} = - \langle L \mathcal{B}_j(s); \mathcal{A}_i(t) \rangle^{\text{eq}}. \quad (7)$$

Here we are interested in the response of $g_i(\{x_k\}, Q_i)$ to the perturbations in (5). Hence, with the identifications $\mathcal{A} = g_i$, $\mathcal{B}_j = g_j$, and $h_j = Q_j - Y_j$, (6) becomes

$$\langle g_i(t) \rangle = \langle g_i \rangle^0 + \sum_{j=1}^M \frac{\beta}{2} \int_{t_0}^t ds [Q_j(s) - Y_j] \times \left[\frac{d}{ds} \langle g_j(s); g_i(t) \rangle^0 - \langle L g_j(s); g_i(t) \rangle^0 \right], \quad (8)$$

where L , the backward generator of the unperturbed dynamics of the environment, reads for (2)

$$L = \mu \sum_{k=1}^N \left[F_k \partial_{x_k} - \lambda \sum_{i=1}^M \partial_{x_k} U_i \Big|_{Q_i=Y_i} \partial_{x_k} + \frac{1}{\beta} \partial_{x_k}^2 \right]. \quad (9)$$

The summands in (8) are the forces due to the linearized fluctuations of the probes around their preferred states. Assuming that the environment was put in contact with the probes at time $t_0 = -\infty$, so that no correlation with the initial conditions is retained, an integration by parts yields

$$\langle g_i(t) \rangle = \langle g_i \rangle^0 + \sum_{j=1}^M \left[G_{ij}(t) - \int_{-\infty}^t ds \zeta_{ij}(t-s) \dot{Q}_i(s) \right]. \quad (10)$$

Here we defined the memory kernel

$$\zeta_{ij}(t-s) \equiv \frac{\beta}{2} \left(\langle g_j(s); g_i(t) \rangle^0 - \int_{-\infty}^s du \langle L g_j(u); g_i(t) \rangle^0 \right), \quad (11)$$

which enters both the friction and the statistical forces mediated by the environment,

$$G_{ij}(t) \equiv [Q_j(t) - Y_j] \zeta_{ij}(0), \quad (12)$$

including the ‘‘self-interaction’’ ($i = j$) and the forces between different probes ($i \neq j$).

Equation (12) establishes the connection between the friction kernel and the fluctuating statistical force, namely

$$\partial_{Q_j} G_{ij} = \zeta_{ij}(0). \quad (13)$$

For $i \neq j$, Eq. (13) relates environment-mediated interactions to cross-friction between probes. It was proposed by De Bacco *et al.* [47] for equilibrium systems arguing on the basis of Onsager’s regression principle. Here we gave a formal proof of this relation that extends its validity to nonequilibrium states.

In equilibrium, where averages are denoted $\langle \dots \rangle^{\text{eq}}$, the frenetic contribution can be eliminated in favor of the entropic term according to (7),

$$\langle g_j(s); g_i(t) \rangle^{\text{eq}} = - \int_{-\infty}^s du \langle L g_j(u); g_i(t) \rangle^{\text{eq}}. \quad (14)$$

We thus retrieve that the friction kernel is a symmetric matrix,

$$\zeta_{ij}(t-s) = \beta \langle g_j(s); g_i(t) \rangle^{\text{eq}} = \zeta_{ji}(t-s), \quad (15)$$

since correlations are functions of $|t - s|$ only, thanks to time-reversal invariance. The symmetry (15) translates into the condition $\partial G_{ij}/\partial Q_j = \partial G_{ji}/\partial Q_i$, which suffices to make g_i derive from an effective (thermodynamic) potential $\mathcal{F}(\{Q_i\})$. That such a potential is the Helmholtz free energy of the environment,

$$\mathcal{F} \equiv -\frac{1}{\beta} \ln \int d\{x_k\} e^{-\beta(\lambda \sum_{i=1}^N U_i + V)}, \quad (16)$$

is easily seen by introducing the Boltzmann factor in (4):

$$\begin{aligned} \langle g_i \rangle^{\text{eq}} &= - \int d\{x_k\} \lambda \partial_{Q_i} U_i e^{-\beta(\sum_{i=1}^N U_i + V - \mathcal{F})} \\ &= \frac{1}{\beta} e^{\beta \mathcal{F}} \partial_{Q_i} \int d\{x_k\} e^{-\beta(\lambda \sum_{i=1}^N U_i + V)} \\ &= \frac{1}{\beta} e^{\beta \mathcal{F}} \partial_{Q_i} e^{-\beta \mathcal{F}} = -\partial_{Q_i} \mathcal{F}. \end{aligned} \quad (17)$$

This ensues the action-reaction principle for the fluctuating forces among probes. Contrarily, when the environment is driven away from equilibrium, (14) is not applicable in general, as frenetic and entropic terms remain distinct. Hence the reciprocal relations are not satisfied, $\zeta_{ij} \neq \zeta_{ji}$, which implies that the action-reaction symmetry is broken.

Now we turn to the random part of the interaction,

$$\eta_i \equiv g_i(\{x_k\}, Q_i) - \langle g_i(\{x_k\}, Q_i) \rangle. \quad (18)$$

It has zero mean by definition, and its two-times correlation is obtained again by application of the response formula (6), with $\mathcal{A} = g_i g_j$,

$$\begin{aligned} \langle \eta_i(t) \eta_j(s) \rangle &= \langle g_i(\{x_k(t)\}, Q_i(t)); g_j(\{x_k(s)\}, Q_j(s)) \rangle \\ &\simeq \langle g_i(t); g_j(s) \rangle^0. \end{aligned} \quad (19)$$

The weak-coupling approximation allowed us to drop higher orders in λ , so that (19) simplifies to

$$\langle \eta_i(t) \eta_j(s) \rangle = \frac{2}{\beta} \zeta_{ij}(t - s) + \int_{-\infty}^s du \langle L g_j(u); g_i(t) \rangle^0. \quad (20)$$

In general, the noise correlation depends explicitly on the excess dynamical activity of the environment, $L g_i$. Yet, in equilibrium, exploiting again the equality of the frenetic and entropic term, (20) reduces to the FDT,

$$\langle \eta_i(t) \eta_j(s) \rangle^{\text{eq}} = \frac{1}{\beta} \zeta_{ij}(t - s). \quad (21)$$

Out of equilibrium (20) cannot be simplified further in general, and the FDT (21) is evidently broken, resulting in asymmetric noise cross-correlations. Such violation of the FDT appears more transparent if (20) is written in terms of the state velocity of the environment, i.e., the vector

$$v(\{x_k\}, \{Q_i\}) \equiv \frac{J(\{x_k\}, \{Q_i\})}{\rho^0(\{x_k\} | \{Q_i\})}, \quad (22)$$

with J the probability current of the environment, which vanishes identically in equilibrium. Even though it could be experimentally estimated [48–52], it has been analytically solved only in a few simple situations in which the stationary distribution is known [28,32,53]. From the identity $L = L^* + 2v \cdot \nabla$ [28,46,54], where ∇ is the vector of partial

derivatives ∂_{x_k} , and L^* is the adjoint of L —the forward generator of the dynamics of the environment—one can easily prove that

$$\begin{aligned} \langle L g_i(u); g_j(t) \rangle^0 &= - \frac{d}{du} \langle g_j(u); g_i(t) \rangle^0 \\ &\quad + 2(v \cdot \nabla g_j(u); g_i(t)) \rangle^0. \end{aligned} \quad (23)$$

Using Eqs. (11), (20), and (23), the broken FDT reads

$$\langle \eta_i(t) \eta_j(s) \rangle = \frac{1}{\beta} \zeta_{ij}(t - s) + \int_{-\infty}^s du \langle v \cdot \nabla g_j(u); g_i(t) \rangle^0, \quad (24)$$

where the deviation from the equilibrium Kubo formula appears explicitly.

In general, the noise (18) will not be Gaussian, and thus the two-times correlation is not enough to fully characterize its statistics. Higher moments can be calculated with the same procedure, though, by successive application of the response formula (6) together with the weak-coupling assumption.

Finally, we note that the restriction of time-independent mean states $\{Y_i\}$ can be easily lifted. If, instead, mean time-dependent trajectories $\{Y_i(t)\}$ are taken, our approach still holds with the caveat that the perturbation potentials, $g_i(\{x_k\}, Y_i(s))$, now carry an explicit time dependence via $Y_i(t)$ [cf. Eq. (5)]. An extension of the response formula (6) needs to be applied [55], which features $\{Y_i(t)\}$ as a quasistatic protocol, but the remaining procedure is very analogous. Therefore, the theory naturally extends to probes that are, e.g., acted upon by external time-dependent forces, or in direct contact with the equilibrium bath, as well as with the environment.

III. EXAMPLES

In this section, we present two explicative examples. First, we consider a single probe coupled linearly to a fluid of non-interacting self-propelled particles. Equations (11) and (20) are calculated analytically and used to show the breakdown of (21). Second, we show how to extract from Brownian simulations the friction memory kernel of two confined probes immersed in a stirred fluid. We prove numerically the breakdown of the reciprocal relations, that is, the violation of the action-reaction principle for the fluid-mediated forces between the probes.

A. One probe in an active fluid

We consider a two-dimensional system ($d = 2$) in which a single probe under harmonic confinement,

$$K(t) = -\kappa_Q [Q(t) - Y], \quad (25)$$

interacts via a harmonic potential U (strength constant κ) with an environment of active Brownian particles [56]. The latter are not mutually interacting but (internally) driven so that they display a drift velocity of constant magnitude v_0 pointing along the random particle orientation $n_k(t)$, i.e.,

$$\mu F(\{x_k\}) = v_0 n_k(t). \quad (26)$$

Due to rotational Brownian motion, the unit vector $n_k(t)$ diffuses with a persistence time D_r [57]:

$$\langle n_k(t) n_{k'}(s) \rangle = \delta_{kk'} e^{-D_r |t-s|}. \quad (27)$$

Therefore, (2) takes the simple form of an Ornstein-Uhlenbeck process with an additional stochastic drift [58]. Thanks to the linearity of the system, the systematic part of the interaction,

$$\langle g \rangle = -\lambda\kappa \sum_{k=1}^N (Q - \langle x_k \rangle), \quad (28)$$

as well as the stochastic part,

$$\eta = -\lambda\kappa \sum_{k=1}^N (\langle x_k \rangle - x_k), \quad (29)$$

can be expressed analytically in terms of Q and Y only. Indeed, the terms in the large square brackets in (8), corresponding to the response function to a constant force,

$$\frac{N\beta\lambda^2\kappa^2}{2} \left[\frac{d}{ds} \langle x_k(s); x_k(t) \rangle^0 - v_0 \langle n_k(s); x_k(t) \rangle^0 + \lambda\kappa\mu \langle x_k(s); x_k(t) \rangle^0 \right], \quad (30)$$

contain simple correlation functions of the unperturbed Ornstein-Uhlenbeck steady state. From (11) we thus obtain the friction kernel

$$\zeta(t-s) = N\lambda\kappa e^{-\lambda\kappa\mu(t-s)}, \quad (31)$$

showing that dissipation happens on the characteristic time scale that it takes the active particles to relax in the coupling potential U . In contrast, the energy input due to the noise (29) is found to occur on multiple time scales,

$$\langle \eta(s)\eta(t) \rangle = \frac{1}{\beta} \zeta(t-s) + \frac{1}{2} \frac{N\lambda\kappa v_0^2}{(\lambda\kappa\mu)^2 - D_r^2} \times \left[\lambda\kappa e^{-D_r(t-s)} - \frac{D_r}{\mu} e^{-\lambda\kappa\mu(t-s)} \right]. \quad (32)$$

The disparity of the time scales for noise and friction entails the breakdown of the FDT, as predicted by (20). One may try to mend it by introducing an effective temperature [59] via

$$\beta T_{\text{eff}}(\tau) = 1 + \frac{\beta v_0^2}{2\mu D_r} \left(1 - \frac{\lambda\kappa\mu}{D_r} e^{-D_r\tau} \right) + O(\lambda^2). \quad (33)$$

Thereby, the FDT (21) is formally restored, albeit with the time-dependent function $T_{\text{eff}}(\tau)$ replacing the constant bath temperature $1/\beta$.

The deviation from equilibrium is seen to be governed by the two dimensionless numbers $\beta v_0^2/2\mu D_r$ and $\lambda\kappa\mu/D_r$. For $\lambda\kappa\mu/D_r \rightarrow 0$, the temperature renormalization becomes time-independent and independent of the weak-coupling parameter λ —it thus acquires the status of thermodynamic temperature. One can then be justified in saying that the probe acts as an ideal measurement device for the constant effective temperature

$$T_{\text{eff}} \sim \beta^{-1} + \frac{v_0^2}{2\mu D_r} \quad (34)$$

of the active fluid itself, which coincides with the known value for a suspension of free active particles [60,61]. The strength of the temperature renormalization is controlled by the Peclet number $v_0(\mu D_r/\beta)^{-1/2}$ that weighs the relative importance

of ballistic versus (translational and rotational) diffusive motion [62].

To first order in λ , Eq. (33) exhibits a crossover from a short-time temperature to a long-time temperature. Moreover, T_{eff} can no longer be interpreted as a property of the particle bath alone, but it characterizes its interaction with the embedded probe. In fact, the ratio $\lambda\kappa\mu/D_r$ can be interpreted as a measure for the interference of the coupling potential with the persistence of the active particle motion. We expect this particular feature to carry over to more general (strongly interacting) systems, where it would not be accessible within the weak-coupling formalism, however. The physical picture is that the apparent thermalization at the constant effective temperature (34) takes some finite time to happen. In our toy model, this “equilibration time” is given by the rotational diffusion time of the active particles, i.e., the active motion of the bath particles can only be subsumed into an enhanced fluid temperature once it has lost its orientational persistence. This very plausible condition has been pointed out before (e.g., in [63]), albeit not for the time domain. If (32) is extrapolated to values of the dimensionless coupling strength on the order of 1, the temporal growth of the corresponding effective temperature takes the form

$$\beta T_{\text{eff}}(\tau) \stackrel{\lambda\kappa\mu \approx D_r}{\approx} 1 + \frac{\beta v_0^2}{4\mu D_r} (1 + \tau D_r). \quad (35)$$

It may tentatively be interpreted as an indication of the onset of strong interactions and collective effects, such as a clustering of the bath particles around the probe, which would entail a progressive heating of the probe. While quantitatively inaccessible to the weak-coupling formalism, corresponding observations have indeed been made in numerical simulations [60,64].

Summing up, we arrived at the generalized Langevin equation for the probe,

$$M \ddot{Q}(t) = -\kappa [Q(t) - Y] - \int_{-\infty}^t ds \zeta(t-s) \dot{Q}(s) + \eta(t), \quad (36)$$

where the friction memory kernel and the noise covariance are given by (31) and (32), respectively. Note that, since n_k is not Gaussian in general, (29) is not Gaussian either. Nevertheless, in view of the central limit theorem, the probability distribution of η converges to a normal one for $N \gg 1$, $\{x_k\}$ being independent identically distributed random variables.

B. Two probes in a stirred fluid

We consider a one-dimensional system ($d = 1$) consisting of $M = 2$ probes under harmonic confinement and $N = 100$ fluid particles moving freely in a periodic domain $x_k \in [0, L]$, as sketched in Fig. 2. The fluid is driven out of equilibrium by an external constant force f that induces a net particle current j thanks to the periodic boundary conditions. The fluid particles interact (mutually and with the probes) through the same soft repulsive potential $V \equiv U$, such that they experience the total force

$$F_k = f - \sum_{k'=1}^N \frac{\partial V_{k'}(x_k, x_{k'})}{\partial x_k}. \quad (37)$$

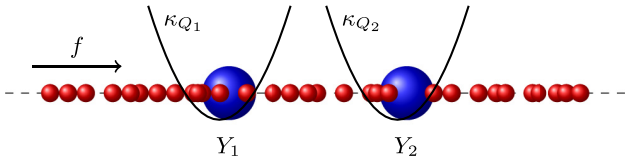


FIG. 2. Schematic illustration of the simulated system, composed of $N + 2$ soft spheres in one spatial dimension with periodic boundary conditions. The probes (blue) have average positions $Y_i \sim Y_i^* + J \int_0^t d\tau \zeta_{ii}(\tau)/\kappa_{Q_i}$, resulting from the balance of the drag force due to the steady current J of fluid particles (red) and to the harmonic confinement with minimum in Y_i^* and stiffness κ_{Q_i} ($i = 1, 2$).

In the following, we present results obtained by using the Gaussian potential

$$V_k(x_k, x'_k) = e^{-\frac{1}{2\sigma^2}(x_k - x'_k)^2}, \quad (38)$$

but we have checked numerically that anharmonic potentials lead to qualitatively similar results. In particular, we have calculated the time-dependent entries of the friction kernel ζ_{ij} from formula (11) for various values of the external driving f . This was done by letting the fluid relax from an initial uniform density, fixing the probes in their preferred positions Y_i , and then performing the steady-state averages in (11) over 2×10^4 independent simulation runs of duration $\mathcal{T} = 10^3$.

For $f \rightarrow 0$, equilibrium conditions are recovered. The diagonal elements ζ_{ii} of the friction kernel are positive and exhibit a monotonic time dependence. The two off-diagonal elements ζ_{12} and ζ_{21} , which quantify the mutual frictional forces between the probes, coincide. As expected, they are negative and decay to zero at late times. Their negative sign can be understood on the basis of global momentum conservation. For example, consider the drag force that probe 1 exerts on probe 2,

$$F_{1 \rightarrow 2}^{\text{drag}} = - \int_{-\infty}^t ds \zeta_{21}(t-s) \dot{Q}_1(s).$$

It is easy to convince oneself that, given the configuration sketched in Fig. 2, a positive velocity \dot{Q}_1 will on average cause a positive displacement of the fluid particles surrounding probe 1. Such perturbation spreads along the coordinate axis reaching probe 2, ultimately resulting in a positive momentum transfer $F_{1 \rightarrow 2}^{\text{drag}} > 0$. This suggests that $\zeta_{21} \leq 0$ for all times.

In contrast, with increasing nonequilibrium force $f > 0$, we observe a qualitative modification of the diagonal and nondiagonal elements of ζ_{ij} , as exemplified in Figs. 3 and 4, respectively. The diagonal elements ζ_{ii} develop a non-monotonic time dependence and eventually turn negative. Physically, this corresponds to a viscoelastic recoiling of the individual probe particles. A more dramatic, genuinely nonequilibrium effect is found for the off-diagonal elements $\zeta_{i \neq j}$. As revealed by Fig. 4, the presence of a nonequilibrium flux in the bath breaks the symmetry of the friction matrix so that $\zeta_{ij} \neq \zeta_{ji}$, with $|\zeta_{21}|$ ($|\zeta_{12}|$) larger (smaller) with respect to equilibrium. Such an effect arises whenever a spatial asymmetry is imposed on top of broken detailed balance. Our periodic system is always spatially asymmetric unless $Y_1 - Y_2 = L/2$. Specifically, in the simulations, the probe

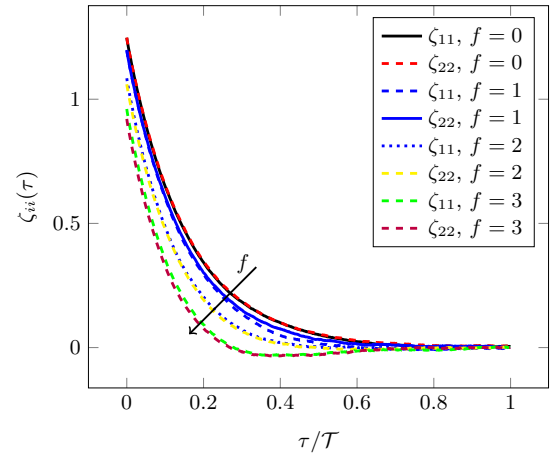


FIG. 3. Diagonal elements of the friction kernel $\zeta_{ii}(\tau)$ as a function of time $\tau = t - s$, obtained by numerical evaluation of (11) in Brownian dynamics simulations, for various values of the nonequilibrium driving force f and $\beta = 1$, $\mu = 1$, and $\sigma = 1$.

reference positions are set to $Y_1 \simeq L/3 < Y_2 \simeq L/2$, and, for convenience, the trap stiffnesses κ_{Q_i} are chosen large enough to make the position Y_i almost coincide with the trap minimum Y_i^* . By increasing L , we checked that interactions with the periodic image particles are negligible. We conclude that global momentum conservation does not hold anymore when the fluid dynamics becomes dissipative. This can be attributed to the asymmetric propagation (due to the current J) of fluid perturbations. Namely, downstream propagation is progressively enhanced by increasing f , while upstream propagation is suppressed. As a result, the influence of probe 1 (2) on probe 2 (1) gets stronger (weaker) as we increase the driving. As for the diagonal elements, the sign of $\zeta_{12}(\tau)$ is transiently reversed. More remarkably, for sufficiently large values of f , the response coefficient of probe 2 to a uniform motion of probe 1, namely $-\int_0^\infty d\tau \zeta_{12}(\tau)$, turns negative. In contrast to the mentioned transient elastic recoil embodied in

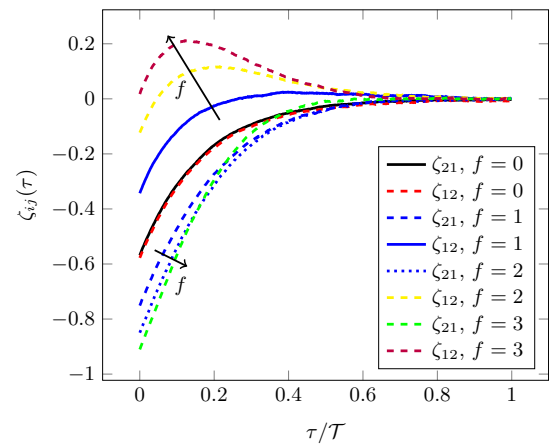


FIG. 4. Off-diagonal elements of the friction kernel $\zeta_{ij}(\tau)$ as a function of time $\tau = t - s$, obtained by numerical evaluation of (11) in Brownian dynamics simulations for various values of the nonequilibrium driving force f and $\beta = 1$, $\mu = 1$, and $\sigma = 1$.

the diagonal terms ζ_{ii} , this kind of “absolute negative mobility” [65–68] is strictly forbidden in equilibrium, where dissipative transport coefficients depend only on the (positive) entropy production but not on the dynamical activity [69].

IV. CONCLUSION

Employing nonequilibrium linear-response theory, we have derived generalized Langevin equations for probe particles interacting with a driven environment. The latter was described by an explicit interacting many-body theory for overdamped colloidal particles representing, e.g., active or sheared colloids. More generally, they can be understood as a set of mesoscopic degrees of freedom. Also, the theoretical framework developed above can be easily adapted to cope with different sources of nonequilibrium (other than the nonconservative force f), such as a nonuniform bath temperature field $\beta(x_k)$.

When only conservative forces are present, our theory correctly reproduces the expected equilibrium properties, i.e., it fulfils the FDT and conforms to Onsager’s regression principle relating the fluctuations of statistical forces to the memory kernel. In general, it extends the Langevin approach into the nonequilibrium realm, predicting the violation of the FDT and the action-reaction law for the fluctuating effective forces. The breaking of these dynamical symmetries is traced back to the mismatch between the excess entropy and dynamical activity induced by probe fluctuations around their preferred states, or, equivalently, to the existence of dissipative currents in the environment. We have shown that these phenomena appear already in simple systems, unless special symmetries are present. Namely, noise and friction felt by a single probe in an active medium do not obey the FDT, except if the relaxation time scales of the system and the fluid are properly tuned, in which case a constant effective temperature can be defined. Also, the cross-frictions between two confined probes in a stirred periodic fluid are dissimilar, and they even change sign with respect to equilibrium whenever the probe reference positions break the spatial symmetry.

The theory allows us to obtain quantitative information about the parameters of the environment from measuring average properties of the probes. For example, from (31) and (32)—which are accessible by measuring, e.g., the spectral density of the probe fluctuations in the trap and its response to a small external kick—the values of the relaxation times $\mu\kappa$ and D_r can be inferred. Conversely, one may even

speculate that some mesoscopic parameters [e.g., $\zeta_{ij}(0)$] might be fixed at will by properly designing the nonconservative driving. This is feasible in principle since formal procedures are available [70] that determine an appropriate environment dynamics conditioned on prescribed mean values [e.g., those entering (11)].

Finally, a remark on the status of the approximation of weak coupling to the nonequilibrium environment seems warranted. In a particle-based theory such as the one we employed, this approximation is explicitly enforced by introducing a small coupling constant λ . Physically, the appropriate values λ may depend on the average number of bath particles with which the probes interact. This should be clear from the example in Sec. III A, where the limit $N \rightarrow \infty$ produces an unphysical divergence of friction and noise strength if λ is not properly scaled. However, in practical applications, the weak coupling is often a dynamical, *emergent*, property resulting from the scale separation between the probe-particle system and the environment. For example, colloidal particles suspended in simple fluids are well described by a linear hydrodynamic theory, although the microdynamics of the fluid molecules is highly nonlinear. This feature is expected to be robust and to survive even far from equilibrium, as long as the driving energy input does not exceed the bath thermal energy [26]. Indeed, the peculiar feature of a time-dependent noise temperature, discovered within the weak-coupling approach mentioned above, was already explicitly demonstrated (and its time dependence analytically computed) in this setting [25].

Recently, new theoretical investigations [71,72] have been spurred by a surge of experimental interest in systems with strongly coupled components, such as in active nonlinear microrheology [73], single-molecule (force spectroscopy) experiments [74], and work extraction from active fluids [75]. Hence, it would be desirable to extend the above analysis to different dynamical descriptions of the environment, i.e., in terms of (hydrodynamic) fields or discrete-state variables. This may provide more versatile formal tools to account more reliably for the weak coupling and to address the strong-coupling problem in a larger variety of stochastic systems.

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Chapter 5

Fluctuation theorems

A tiny glimpse into the fog of nonequilibrium physics has been caught in the preceding chapters. We have seen that the Brownian scale separation allows for the coarse-graining of driven degrees of freedom. That Markovian dynamics (together with local detailed balance) entail nonequilibrium virial relations and thus generalized equations of state. That stochastic descriptions allow to develop linear response theory of nonequilibria and permit to rationalize its dissipative and dynamical aspects. All these findings potentially shed light on several nonequilibrium processes happening in a wealth of physical systems. Yet, their domain of applicability is constrained by the dynamical hypothesis they rest on, whose validity needs to be assessed on a case-by-case basis. In this last chapter we are going to take a small step toward universality, treating a broad class of nonequilibrium results called fluctuations theorems. We will see that they are ultimately based on microscopic symmetries—as the most profound laws of physics are—that endow them with a remarkable generality.

With the name fluctuation theorems [59, 131, 139–152], or fluctuation relations (FRs), one usually denotes symmetry relations holding in irreversible processes for the statistics of thermodynamic quantities, such as entropy production and work. They are valid for classical as well as quantum systems [153–157], driven arbitrarily far from equilibrium, mostly irrespective of their precise (deterministic or stochastic) dynamical laws. It is the underlying time-reversal invariance of the microphysics¹, broken by superimposing nonequilibrium conditions, that makes them so largely applicable to situations as diverse as electron/photon counting in nano-devices [158] to single molecules force spectroscopy experiments [159].

In plain words, the FRs deals with rare events happening out of equilibrium and quantify their relative likelihood in both macro- and microscopic systems. But, it is the mesoscopic realm where they become relevant and useful. For example, take the spontaneous cooling down of an ice cube in the sunlight. On the one hand, such spontaneous flow of heat from cold to hot is prohibited by the second law of thermodynamics. On the other, while certainly unexpected, it is a possible process legitimated by time reversibility of Newton’s law. To reconcile the two views, one should recall that thermodynamic statements applies only to large scales². Hence, we could imagine this to happen to a minuscule ice cube on a tiny time interval. This, i.e. the unusual fluctuations that abound in the mesoscopic world, is what the FRs are all about.

¹For now we exclude from our discussion some more recent forms of FRs which are based on different symmetries, e.g., spatial ones, which are non-universal but rather peculiar to any specific system. We will come to that later.

²Namely, to systems composed of many constituents and to times much longer than the characteristic microscopic timescales.

Let us expose the core content of FRs, without entering here into any specific (let alone, rigorous) formulation. Assume that \mathcal{X} is one realization of a physical process, made up by a time-ordered sequence of events, that lasts for a time t . Imagine we can reproduce it very many times in a controlled experiment, so as to obtain a good estimate for the probability to observe such process, $P[\mathcal{X}]$. Having recorded the experiment outcome, we can play backward in time any given sequence of events \mathcal{X} , and name this new process $\bar{\mathcal{X}}$. If enough data were collected, we can construct from the occurrence frequency of $\bar{\mathcal{X}}$ its associated probability $P[\bar{\mathcal{X}}]$. Under equilibrium conditions, what we will observe is detailed balance, namely, equal probability of forward and backward processes, $P[\mathcal{X}] = P[\bar{\mathcal{X}}]$. In this case, the time reversibility of the microscopic dynamics, is lifted up to the mesoscopic level where our experiment is performed, so that no preferred direction in time is identifiable. Instead, when nonequilibrium conditions are imposed, the emergent irreversibility manifests as a difference in the observed probabilities, in the form

$$P[\mathcal{X}] = P[\bar{\mathcal{X}}] \exp(tf[\mathcal{X}]), \quad (5.1)$$

where $f[\mathcal{X}]$ is a functional measuring the dissipation rate in the process—hence it changes sign under time reversal. Equation (5.1), a master relation from which all FRs descend, implies that a process \mathcal{X} with positive dissipation is exponentially more likely than the time-reversed $\bar{\mathcal{X}}$, which actually becomes unobservable in the long run ($t \rightarrow \infty$). This expected thermodynamic behavior is then capture by summing (5.1) over all processes,

$$\langle \exp(-tf) \rangle = 1 \implies \langle f \rangle \geq 0. \quad (5.2)$$

Such inequality is clearly reminiscent of the second law of thermodynamics. How exactly the dissipation is accounted for in f , and how the different versions of FRs unfold from (5.1), depends on the dynamics modeling the process \mathcal{X} and the initial conditions from which it originates. These factors have for some time hampered to recognize the essential unity of the various FRs.

The FRs initially appeared as scattered results in different contexts, starting in 1993 with the seminal work of Evans et al. on the fluctuations of the entropy production of a deterministic particle system under shear, modeling a constantly sheared fluid [141]. Very soon, FRs were proved for equilibrium initial conditions perturbed by arbitrary large dissipative forces [59], as well as for steady conditions [142, 143]. These results hold for deterministic time-symmetric dynamics, where the interaction of the system with the thermal bath is modeled by *ad hoc* thermostats, i.e. artificial forces (replacing the very many degrees of freedom of a real bath) which fix some macroscopic observable, like kinetic or total energy [121, 160]. These forces, having non-Hamiltonian nature, do not preserve the phase space volume³. For any set of conjugate variables $\{q_i, p_i\}_{i=1}^N$, the negative divergence of the equations of motion, $-\sum_{i=1}^N [\partial_{q_i} \dot{q}_i + \partial_{p_i} \dot{p}_i] \equiv \sigma$, quantifies how much volumes in phase space shrink and somewhat reveals how dissipative the system is. It is indeed σ which enters the deterministic FR (5.1), as $f[\mathcal{X}] \sim \int^t dt' \sigma/t$. Given the existence of a correspondence⁴ between σ and the entropy production rate, this (apparently abstract) result acquires a clear thermodynamic significance [161].

³Recall that Hamiltonian flows are incompressible, i.e. the Liouville theorem ensues the conservation of phase space volumes.

⁴We cannot refrain from mentioning that such correspondence is complete when initial conditions are taken into account, as in the transient Evans-Searles FR. Instead, when σ is taken alone, as it happens for the steady-state Gallavotti-Cohen FR, it is related to entropy production only for some specific choices of the thermostating forces [123].

As one may imagine, the rigorous approach based on deterministic FRs for the entropy production is mathematically involved. It makes large use of concepts from dynamical systems theory, exploiting the connection between the contraction rate and the Lyapunov exponents, i.e. the divergence rates of microscopic nearby trajectories [162]. In particular, the theory by Gallavotti and Cohen rests on very stringent conditions (in general not verifiable [123]) on the chaotic properties of a system, which the authors have elevated to the rank of a founding hypothesis. It is the so called *chaotic hypothesis*, whose role is argued to parallel that of the ergodic hypothesis in equilibrium statistical mechanics [142, 143]. Here we do not dwell on this subject, pointing the interested reader to [100], where we review part of the fundamental concepts precluding a rigorous treatment of deterministic FR.

The interest in FRs for the entropy production grew larger when stochastic formulations appeared which were based on the Langevin and master equations [146, 149]. Thanks to their (relative) mathematical simplicity and the versatility in describing diverse mesoscopic systems, the research on stochastic FRs flourished. The developments improved the understanding of stochastic energetics [78] and led to a complete fluctuating thermodynamic theory through the identification⁵ of a trajectory-dependent system entropy $s \equiv -\log \rho$ [151]. Indeed, upgrading the Gibbs definition of (mean) entropy to nonequilibrium probability distributions $\rho(x, t)$, i.e. $-\int dx \rho(x, t) \log \rho(x, t) = \langle s(x, t) \rangle$, and regarding $s(x(t), t)$ as a trajectory function, permits to fully identify the dissipation f appearing in (5.1) as the total entropy production in the universe [151]. It amounts to an extensive contribution stemming from the heat Q flowing into the heat bath, plus a boundary contribution coming from a variation of the system entropy:

$$k_B t f[\mathcal{X}] = Q/T + s(x(t), t) - s(x(0), 0). \quad (5.3)$$

Other results, known as work relations, can be equally fit into this framework. The most prominent is the Jarzynski equality [144, 145, 163], originally proved for Liouvilian dynamics, which connects the work W and free-energy variations ΔF in systems prepared in equilibrium and manipulated at arbitrary speed,

$$\langle e^{-W/k_B T} \rangle = e^{-\Delta F/k_B T}. \quad (5.4)$$

The subsequent extension by Crooks clarified the common origin of this and previous FRs [147, 148], traced back to the breaking of time reversal. In particular, one obtains the Jarzynski equality from (5.3), using the first law $\mathcal{H} = -Q + W$, with \mathcal{H} the system Hamiltonian, and calculating the difference in system entropy between two canonical states, $s(x(t), t) - s(x(0), 0) = (\Delta \mathcal{H} - \Delta F)/T$.

Due to the differences exposed above, the research on deterministic and stochastic FRs has proceeded along divergent paths, in general. In our contribution [58] we propose an analogy between the results based on these different dynamics. Because the former consists of dynamical equations which are not time-symmetric—time-symmetry exists in the probability space of trajectories by enforcing local detailed balance condition—, it is clear that other transformations than time inversion are to be employed in order to match the results based on deterministic dissipative equations. We thus consider an auxiliary transformation which changes the sign of the friction

⁵In dissipative deterministic systems, assigning an entropy to the system itself is problematic. For example, the Gibbs/Shannon definition of entropy requires the existence of a smooth probability density ρ in phase space. This is not the case for dissipative deterministic systems whose phase space probability shrinks in the long run into attractors of null measure [123].

coefficient, thus simulating the time-symmetry of the deterministic thermostats. Such artificial transformation suffices to single out the dissipation function and thus yields the (integrated) FR originally found by Evans and Searls, once the auxiliary transformed dynamics is traced out. Exploiting the correspondence, we interpret the FR in continuous systems described by Langevin equations as symmetry relations for their Lyapunov spectrum. We then carry over the analogy to systems described by master equations, where the auxiliary dynamics is actuated by inverting the transition rates, and propose a concept equivalent to phase space contraction rate in systems with discrete states. On top of unraveling formal and conceptual similarities between stochastic and deterministic systems, [58] highlights the possibility to obtain FRs for physical quantities not necessarily related to irreversibility. The importance of dynamical, i.e. time-symmetric, aspects for the understanding of nonequilibria is nowadays fully recognized [45, 164] and, indeed, it has been one central topic in Chapter 4.

So far we have stressed the unity of FRs whose common origin is rooted in the (broken) time-symmetry of microscopic laws. However, if considered in a broader context, time reversal is not special among all the possible space-time symmetries of physics. Think about a system of particles interacting via forces depending on the relative distance. Clearly, a global translation or rotation leaves the system invariant, a property that may be broken adding, e.g., an external (dissipative) field. It was indeed realized that any spacial symmetry can be used to identify statistical properties of specific vectorial quantities, namely, the system's currents, as much as time reversal is used to assess a scalar quantity like entropy production. For isotropic systems, the spatial FR gives a direct relation between the probability of a system to be traversed by two currents of equal magnitude pointing in different directions [165–167]. Importantly, it restricts the possible statistical properties of nonequilibrium systems. And it does so in a very insightful way, since it implies a set of hierarchies for nonlinear response coefficients in terms of the current cumulants [165].

Spurred by their conceptual and practical relevance, in [57] we have verified the validity of the FRs for the entropy production and currents in experiment and computer simulations of a self-thermophoretic colloid. This is a particular instance of self-propelled particle, which converts the inhomogeneous heating caused by irradiated laser light into directed motion, at the expense of continuous dissipation in the solvent. The existence of long-lived (partly unknown) nonequilibrium fluctuations in the inhomogeneous solvent and the inherent stochasticity of the driving are found to have little bearing on the FRs. On the contrary, the paper's results highlight the central role of symmetries for the validity of the FRs and the little relevance of the exact knowledge of dynamical rules.



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About the role of chaos and coarse graining in statistical mechanics



G. Falasco^a, G. Saggiorato^{b,*}, A. Vulpiani^c

^a Institut für Theoretische Physik, Universität Leipzig, Postfach 100920, Leipzig 04009, Germany

^b Theoretical Soft Matter and Biophysics, Institute of Complex Systems and Institute for Advanced Simulation, Forschungszentrum Jülich, 52425 Jülich, Germany

^c Department of Physics, University of Roma "Sapienza", P.le A. Moro 2, I-00185 Roma, Italy

HIGHLIGHTS

- We discuss the role of ergodicity and chaos for the validity of statistical laws.
- We explore the basic aspects of chaotic systems on systems composed of a huge number of particles.
- We emphasize on the finite-resolution aspects.

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ABSTRACT

We discuss the role of ergodicity and chaos for the validity of statistical laws. In particular we explore the basic aspects of chaotic systems (with emphasis on the finite-resolution) on systems composed of a huge number of particles.

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1. Introduction

Statistical mechanics was founded by Maxwell, Boltzmann and Gibbs to account for the thermodynamics of macroscopic bodies, i.e. systems with a very large number of particles, starting from the microscopic interactions. The typical claim is that statistical mechanics works without very precise requirements on the underlying dynamics (except for the assumption of ergodicity). With the discovery of deterministic chaos it became clear that statistical approaches may also be unavoidable and useful in systems with few degrees of freedom. However, even after many years there is no general agreement among the experts about the fundamental ingredients for the validity of statistical mechanics.

The wide spectrum of positions ranges from the belief of Landau and Khinchin in the main role of the many degrees of freedom and the (almost) complete irrelevance of dynamical properties, in particular ergodicity, to the opinion of those, for example Prigogine and his school, who consider chaos as the basic ingredient.

For almost all practical purposes one can say that the whole subject of statistical mechanics consists of the evaluation of a few suitable quantities (for example, the partition function, free energy, correlation functions). The ergodic problem is often forgotten and the (so-called) Gibbs approach is accepted because “it works”. Such a point of view cannot be satisfactory, at least if one believes that it is not less important to understand the foundation of such a complex issue than to calculate useful quantities.

* Corresponding author. Tel.: +49 2461613913.
E-mail address: g.saggiorato@fz-juelich.de (G. Saggiorato).

The present paper is meant to serve as a short informal introduction to the problem of the connection between dynamical behavior (mainly ergodicity and chaos) and statistical laws.

This contribution has been written by G.S. and G.F from the lectures delivered by A.V.

2. The bridge to statistical mechanics

Before moving on to a more technical discussion we want to elucidate the pivotal role played by ergodicity in passing from a mechanical to a statistical description of a macroscopic system. Let us consider an isolated system of N particles. Denoting by \mathbf{q}_i and \mathbf{p}_i the position and momentum vectors of the i th particle, the state of the system at time t is described by the vector $\mathbf{x}(t) = (\mathbf{q}_1(t), \dots, \mathbf{q}_N(t), \mathbf{p}_1(t), \dots, \mathbf{p}_N(t))$ in a $6N$ -dimensional phase space. The evolution law is given by Hamilton's equations. Given a physical observable $A(\mathbf{x})$, its time average over a period T is defined by:

$$\bar{A}^T(\mathbf{x}(0)) = \frac{1}{T} \int_0^T A(\mathbf{x}(t)) dt. \quad (1)$$

In general (1) is a function of the averaging time T and of the initial conditions $\mathbf{x}(0)$. We assume that \bar{A}^T is the result of an experimental measurement, i.e. is performed on a macroscopic time T . Therefore, since T is much larger than the microscopic dynamics time scale over which the molecular changes occur, the formal limit $T \rightarrow \infty$ can be considered. We say that the ergodic hypothesis is satisfied if the time average

$$\bar{A} \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(\mathbf{x}(t)) dt, \quad (2)$$

is a function of the energy only, independent of the initial conditions. If it is the case, the time average (2) can be replaced by the probability average

$$\bar{A} = \int \rho_{\text{mc}}(\mathbf{x}) A(\mathbf{x}) d\mathbf{x} \equiv \langle A \rangle, \quad (3)$$

where $\rho_{\text{mc}}(\mathbf{x})$ is the micro-canonical probability density function, defined constant over a constant energy surface. The validity of (3) constitutes the main question of the ergodic problem. In the following we address the issue of identifying the conditions under which a dynamical system is ergodic. It will soon be clear that mathematical ergodicity is extremely difficult to be asserted and, in fact, weaker properties can be required to physical systems.

Let us wonder about the basic question of the foundation of the statistical mechanics: why do the time averages of the microscopic properties of a system of particles describe the thermodynamic properties of the object composed of those particles? The microscopic system, in fact, consists of a myriad of mechanical parameters, such as the particles, energy and momentum, while thermodynamics consists of just a few measurable quantities, like temperature and pressure. The corresponding diversity of fundamental terminology, qualifies the reduction of thermodynamics to mechanics as “heterogeneous” reduction [1], a condition which may prevent the logical derivation of the former theory from the latter. For such a problem the typical approach of the philosophy of science is to require the existence of relations between the terms of the mechanics and elements of the vocabulary of thermodynamics. Such bridge law must reflect a kind of identity between the objects of study of the two theories [1]. The bridge law which associates thermodynamics with the classical mechanics of atoms was proposed by Boltzmann and it is engraved in his tomb stone:

$$S = k \log W. \quad (4)$$

This celebrated relation connects the thermodynamic entropy S of an object in the macroscopic state X , to the volume W of all microstates correspond to the same X . For example, considering the macrostate X corresponding to a given energy E , one typically considers the energy shell $E - \delta E \leq H(\{\mathbf{q}_n\}, \{\mathbf{p}_n\}) < E$, with small δE , and obtains:

$$W = \int_{E - \delta E \leq H(\mathbf{q}, \mathbf{p}) < E} d\mathbf{q}_1 \dots d\mathbf{q}_N d\mathbf{p}_1 \dots d\mathbf{p}_N.$$

The micro-canonical probability distribution is constant (equal to $1/W$) in the energy shell and zero otherwise. Eq. (4) qualifies as a bridge law, because S is a thermodynamic quantity, while W is a microscopic entity. Once it has been introduced, further mechanical properties of our description of the microscopic dynamics may be related to as many other thermodynamic quantities, thus bridging the gap between micro- and macro-descriptions.

3. Some general considerations about ergodicity

Here we introduce the notion of dynamical system:

Definition (Dynamical System). A deterministic dynamical system is described by the triplet (Ω, S^t, μ) , where:

- Ω is the phase space containing the system state vector \mathbf{x} ;
- S^t is the evolution operator: $\mathbf{x}(t) = S^t \mathbf{x}(0)$;
- μ is a measure invariant under the evolution S^t , i.e. $\mu(G) = \mu(S^{-t}G)$ for all $G \subset \Omega$.

The consideration of the previous section naturally extends to a generic dynamical system, leading to the following definition of ergodicity [2]:

Definition (Ergodicity). The dynamical system (Ω, S^t, μ) is called ergodic with respect to the invariant measure $\mu(\mathbf{x})$, if, for every integrable function $A(\mathbf{x})$ and for almost all initial conditions $\mathbf{x}(0)$, one has:

$$\bar{A} \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(S^t \mathbf{x}(0)) dt = \int A(\mathbf{x}) d\mu(\mathbf{x}) \equiv \langle A \rangle. \quad (5)$$

We note that in conservative systems (as the isolated Hamiltonian system of the previous section) the invariant measure can be written in terms of a density, i.e. $d\mu(\mathbf{x}) = \rho(\mathbf{x})d\mathbf{x}$, while in dissipative systems it cannot, being singular with respect to the Lebesgue measure due to the shrinking of space phase volumes.

On an abstract level, necessary and sufficient conditions for a dynamical system to be ergodic are given by the Birkhoff theorem [3]:

Theorem (Birkhoff).

- For almost every initial condition $\mathbf{x}(0)$ the following time average exists:

$$\bar{A}(\mathbf{x}(0)) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(S^t \mathbf{x}(0)) dt. \quad (6)$$

- The system is ergodic if, and only if, Ω cannot be subdivided into two invariant parts each of positive measure.

Since in general it is not possible to decide whether a given system satisfies the above hypothesis, the Birkhoff theorem is of scarce practical relevance in connection with statistical mechanics. Also, since the limit $T \rightarrow \infty$ in (6) is just formal, one should ask oneself how large T has to be taken in practice in order to get a fair convergence of time and ensemble averages. It turns out that, for microscopic observables, T is of the same order of the Poincaré recurrence time. As a simple example we consider a phase space region $G \subset \Omega$ and the observable

$$B(\mathbf{x}) = \begin{cases} 1 & \text{if } \mathbf{x} \in G, \\ 0 & \text{otherwise.} \end{cases} \quad (7)$$

We call $B(\mathbf{x})$ a microscopic observable because the exit of a single particle from G causes a variation of $B(\mathbf{x})$ of the same order of its value. The time average \bar{B}^T is the fraction of time spent by the system in G during the interval $[0, T]$, and it approaches $\mu(G)$ when $T \rightarrow \infty$. Clearly, the time needed to have a good agreement of \bar{B}^T with $\langle B \rangle$ is of the order of the time, denoted $\langle \tau(G) \rangle$, it takes the system to explore the phase space and to come back to G . Thanks to the *Kac lemma* we can express this mean recurrence time as [4]:

$$\langle \tau(G) \rangle = \frac{\tau_0}{\mu(G)},$$

where τ_0 is a characteristic time of the system. Assuming G to be a $6N$ -dimensional hypercube of edge l_G in a phase space of characteristic dimension $L > l_G$, we can use the estimation $\mu(G) \sim (l_G/L)^{6N}$ to obtain:

$$\langle \tau(G) \rangle \sim \tau_0 \left(\frac{L}{l_G} \right)^{6N}. \quad (8)$$

From (8) we conclude that, in macroscopic systems, time averages of some microscopic quantity must be performed for times T much larger than the age of the Universe in order to be in accordance with ensemble averages.

Nevertheless, it must be recognized that the approach we have adopted so far, consisting in proving ergodicity for generic systems and observables, is quite demanding and in fact not useful for the purpose of justifying the statistical approach. In this regard, it is more reasonable to require ergodicity to hold in the weaker form

$$\bar{A} = \langle A \rangle + O(\epsilon) \quad \text{with } \epsilon \ll 1, \quad (9)$$

after having introduced the following assumptions:

- the system is macroscopic, i.e. composed of $N \gg 1$ particles;
- Eq. (9) is valid for physical observables, not for all generic functions.
- Eq. (9) is valid for initial conditions $\mathbf{x}(0) \in \Omega - G$, with $\mu(G) \ll 1$.

The validity of (9) for specific macroscopic observables and a particular class of Hamiltonian systems is ensured by the Khinchin theorem [5]:

Theorem (Khinchin). In a separable Hamiltonian system

$$H = \sum_{n=1}^N H_n(\mathbf{q}_n, \mathbf{p}_n), \quad (10)$$

observables of the form

$$A(\mathbf{x}) = \sum_{n=1}^N A_n(\mathbf{q}_n, \mathbf{p}_n), \quad \text{with } A_n = O(1), \quad (11)$$

satisfy the relation

$$\text{Prob} \left(\frac{|\bar{A} - \langle A \rangle|}{|\langle A \rangle|} \geq C_1 N^{-1/4} \right) \leq C_2 N^{-1/4}, \quad \text{with } C_1, C_2 = O(1). \quad (12)$$

Essentially, the Khinchin theorem states the following: in a system of non-interacting particles, for the sum functions (11) (e.g. pressure, kinetic energy, single particle distribution), the set of points for which time and ensemble averages differ more than a given amount, which goes to zero as $N \rightarrow \infty$, has a measure which goes to zero as $N \rightarrow \infty$.

Furthermore, under the assumptions (10) and (11) it is possible to prove that the relation (12) holds true even substituting $\bar{A} \rightarrow A$, i.e. physically relevant observables are in practice constant on a constant energy surface. This amounts to the stronger statement that statistical mechanics' approach, based on ensemble averages, is in fact independent of (mathematical) ergodicity. Its validity is purely a consequence of the large number of degrees of freedom of microscopic systems [6].

A weak aspect, from the physical point of view, of Khinchin's approach concerns the no-interaction assumption. In contrast, an essential requisite for thermodynamic behavior is the possibility of an exchange of energy among the particles. Of course Khinchin noted the problem and argued that the actual Hamiltonian is indeed only approximated by the separable Hamiltonian. The feeling of Khinchin was that the interaction among the particles contributes very little to evaluate the averages and for the majority of computations in statistical mechanics one can neglect these terms. The undesirable restriction to the separable structure of the Hamiltonian, was removed by Mazur and van der Linden [7]. They extended the result to systems of particles interacting through a short-range potential, showing that the intuition of Khinchin, that the interaction among the particles is of little relevance, was basically correct.

4. Non-integrable systems and the ergodic problem

The issue of ergodicity is related to the problem of the existence of conserved quantities, also called first integrals, in Hamiltonian systems. Indeed, as integrable systems are non-ergodic, a natural question is whether non-integrability implies ergodicity.

First we recall the notion of integrable system:

Definition (Integrable System). A system, described by the Hamiltonian $H(\mathbf{q}, \mathbf{p})$ with $\mathbf{q}, \mathbf{p} \in \mathbb{R}^N$, is called integrable if there exists a canonical transformation from the variables (\mathbf{q}, \mathbf{p}) to the action-angle variables $(\mathbf{I}, \boldsymbol{\theta})$, such that the new Hamiltonian takes the form $H = H_0(\mathbf{I})$, i.e. it depends only on the action \mathbf{I} .

The time evolution of an integrable system is given by:

$$\begin{cases} \dot{\mathbf{I}} = -\frac{\partial H_0}{\partial \boldsymbol{\theta}} = \mathbf{0} \implies \mathbf{I}(t) = \mathbf{I}(0), \\ \dot{\boldsymbol{\theta}} = \frac{\partial H_0}{\partial \mathbf{I}} = \boldsymbol{\omega} \implies \boldsymbol{\theta}(t) = \boldsymbol{\theta}(0) + \boldsymbol{\omega}(\mathbf{I}(0))t. \end{cases} \quad (13)$$

Hence, integrable systems have N independent first integrals, as the action \mathbf{I} is conserved and the motion evolves on N -dimensional tori T_n . Of course, from (13) it follows that $\boldsymbol{\theta} = \boldsymbol{\theta}(0)$, which in general cannot coincide with $\langle \boldsymbol{\theta} \rangle$, integrable systems are evidently non-ergodic. Consequently, it is natural to wonder about the effect of a perturbation $\epsilon H_1(\mathbf{I}, \boldsymbol{\theta})$ on H_0 , and whether the perturbation allows for the existence of first integrals besides the energy. Clearly, that would maintain the perturbed system non-ergodic. This possibility is ruled out by the Poincaré result [8]:

Theorem (Poincaré). Consider a system described by the Hamiltonian

$$H(\mathbf{I}, \boldsymbol{\theta}) = H_0(\mathbf{I}) + \epsilon H_1(\mathbf{I}, \boldsymbol{\theta}). \quad (14)$$

If $\epsilon = 0$ the system has N first integrals \mathbf{I} . Whereas, if $0 < \epsilon \ll 1$, the system does not allow analytic first integrals, apart from energy.

The sketch of the proof goes as follows. We introduce the function

$$\mathbf{F}(t) = \mathbf{I} + \sum_m \epsilon^m \mathbf{F}_m(t), \quad (15)$$

and require it to be a first integral, i.e.

$$\frac{d\mathbf{F}}{dt} = \{H, \mathbf{F}\} = \mathbf{0}, \quad (16)$$

where $\{., .\}$ denotes the Poisson bracket. Inserting (15) into (16) one obtains, for the lower meaningful order $O(\epsilon)$, the equation:

$$\{H_0, \mathbf{F}_1\} + \{H_1, \mathbf{I}\} = \mathbf{0}. \quad (17)$$

If one expresses H_1 and F_1 as Fourier series in the angle vector θ :

$$H_1(\mathbf{I}, \theta) = \sum_{\mathbf{k}} c_{\mathbf{k}}(\mathbf{I}) e^{-i\mathbf{k}\cdot\theta}, \quad \mathbf{F}_1(\mathbf{I}, \theta) = \sum_{\mathbf{k}} \mathbf{f}_{\mathbf{k}}(\mathbf{I}) e^{-i\mathbf{k}\cdot\theta},$$

Eq. (17) yields after some algebra:

$$\mathbf{f}_{\mathbf{k}}(\mathbf{I}) = \frac{c_{\mathbf{k}}(\mathbf{I})\mathbf{k}}{\boldsymbol{\omega}_0(\mathbf{I}) \cdot \mathbf{k}}, \quad (18)$$

where $\boldsymbol{\omega}_0(\mathbf{I}) = \frac{\partial H_0}{\partial \mathbf{I}}$ is the unperturbed frequency vector. Clearly, since the denominator of (18) can be arbitrary small, $\mathbf{f}_{\mathbf{k}}$ may be divergent. Therefore, one concludes that first integrals, except for energy, cannot exist.

Nonetheless, it is not correct to infer from the Poincaré result, as it happened historically [9], that the Hamiltonian system (14) becomes ergodic as soon as $\epsilon \neq 0$. A proof of the fact that non-integrability does not imply ergodicity is indeed given by the Kolmogorov–Arnold–Moser (KAM) theorem [10,11].

Theorem (KAM). *Given the Hamiltonian $H(\mathbf{I}, \theta) = H_0(\mathbf{I}) + \epsilon H_1(\mathbf{I}, \theta)$, with H_0 sufficiently regular and $\det \left| \frac{\partial^2 H_0(\mathbf{I})}{\partial I_i \partial I_j} \right| \neq 0$, if $\epsilon \ll 1$, then, on the constant-energy surface, invariant tori T_n^* survive in a region whose measure tends to 1 as $\epsilon \rightarrow 0$. The tori T_n^* correspond to the tori T_n of H_0 with deformations of order $O(\epsilon)$.*

Therefore, the KAM theorem explains the lack of first integrals, revealed by the Poincaré result, with the local destruction of the (unperturbed) periodic orbits and, consequently, proves that small perturbations are in general not sufficient to provide ergodicity. In the next section we introduce a paradigmatic example of a nearly-integrable system, namely the Fermi–Pasta–Ulam chain, and qualitatively explain its properties in terms of the KAM theorem.

4.1. The Fermi–Pasta–Ulam problem

Fermi, Pasta and Ulam (FPU) investigated the time evolution of a chain of non-linear oscillators with pinned ends [12]. Their primary interest was the thermalization time, i.e. the time needed by the system to lose memory of the initial conditions. In fact, since the non-linear forces render the system non-integrable, the physicists' community expected the system to display ergodic properties. This widespread belief was due to the conclusion, erroneously drawn by Fermi in view of the Poincaré result [9], according to which non-integrability should have implied ergodicity. The study of the FPU system first revealed the pitfall of this rationale, that later was better understood in the light of the KAM theorem.

The Hamiltonian considered in the FPU problem is:

$$H = \sum_{n=0}^N \left[\frac{p_n^2}{2m} + \frac{k}{2} (q_n - q_{n-1})^2 + \frac{\epsilon}{r} (q_n - q_{n-1})^r \right], \quad (19)$$

where ϵ is a perturbation parameter and $r = 3$ or $r = 4$. For $\epsilon = 0$, the Hamiltonian (19) is integrable and can be written as

$$H_0 = \sum_{n=0}^N \left(\frac{\dot{A}_n^2}{2} + \frac{\omega_n^2}{2} A_n^2 \right), \quad (20)$$

by exploiting the normal modes:

$$A_n = \sqrt{\frac{2}{N+1}} \sum_j q_j \sin \left(\frac{n\pi j}{N+1} \right).$$

Needless to say, the Hamiltonian (20) describes a system of decoupled harmonic oscillators with angular frequencies ω_n expressed by

$$\omega_n = \sqrt{\frac{4k}{m}} \sin \left(\frac{n\pi}{2(N+1)} \right).$$

For $\epsilon \ll 1$ one can compute the equilibrium value of all the thermodynamic quantities as averages over a statistical ensemble. In particular, the energy per mode $\langle E_n \rangle$ is:

$$\langle E_n \rangle = \frac{E_0}{N} + O(\epsilon),$$

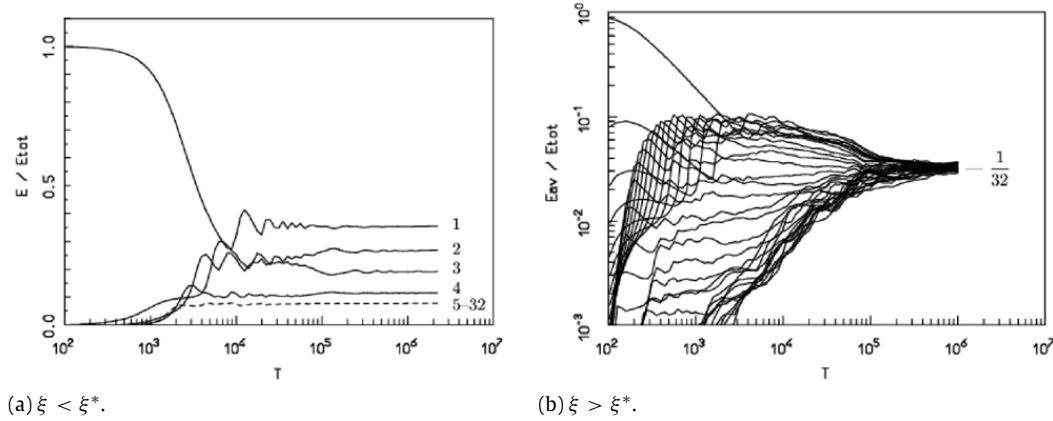


Fig. 1. Time-averaged energy per mode for the FPU systems with parameters $r = 3$, $\epsilon = 0.1$, $N = 32$ and energy densities $E/N = 0.07$ (1a) and $E/N = 1.2$ (1b). In both cases the initial conditions are: $E_1(0) = E_0$ and $E_n(0) = 0$ for $n \geq 2$. Before the results on the FPU system, it was expected that the time-averaged energy of each mode converges to the ergodic value of E_0/N . This is not true when the energy density is smaller than a characteristic value ξ^* that depends on the size system and the perturbation intensity.

which is nothing but the energy equipartition law. Of course, with $\epsilon = 0$ the time average computed along a (sufficiently long) trajectory, $\overline{E_n}$, cannot in general coincide with $\langle E_n \rangle$ since different modes, being uncoupled, maintain their initial energy. Instead, with $\epsilon > 0$ the expectation was to retrieve the equality $\langle E_n \rangle = \overline{E_n}$ whatever the initial conditions $E_n(0)$, even as weird as the one with excitation only in the first mode: $E_1(0) = E_0$ and $E_n(0) = 0$ for $n \geq 2$ [13,14]. However, numerical integration of (19) for fixed N , $\epsilon > 0$, and small energy density $\xi = E/N$ proved this expectation wrong (see Fig. 1).

Namely, there exists a threshold value of the perturbation parameter, ϵ_c , function of N and the initial conditions, which separates the following two regimes:

- if $\epsilon < \epsilon_c$, irrespective of the observation time, $\overline{E_n}$ depends on the initial conditions.
- if $\epsilon > \epsilon_c$, $\overline{E_n}$ converges to the ergodic value $\langle E_n \rangle$.

Notice that, when one deals with realistic working cases, the intensity of the perturbation is, usually, part of the model, i.e. not a control parameter. In these cases the control parameter can be the energy density, and a similar minimum value of ξ exists.

These results can be seen as a verification of the KAM theorem [6]: when $\epsilon < \epsilon_c$ some of the invariant tori of the constant energy surface of the unperturbed system survive the perturbation and result in deformed tori. If the number of degrees of freedom is smaller than $N = 2$, the tori separate regions of the phase space where, in principle, the system can show different behaviors. When the number of degrees of freedom is bigger than 2, the complement set of the tori is connected, allowing for a *diffusing* behavior among all the phase space, excluded the tori, called the Arnold-diffusion [15].

4.2. Is chaos necessary for the validity of the statistical mechanics?

To proceed further we introduce the useful concept of the Lyapunov exponent. The Lyapunov exponent characterizes how much sensitive a system is with respect to initial conditions, quantifying the growth rate of the separation of trajectories initially at distance $\delta(0) \rightarrow 0$.

Definition (Lyapunov Exponent). The first, or maximal, Lyapunov exponent of the dynamical system (Ω, S^t, μ) is:

$$\lambda = \lim_{t \rightarrow \infty} \lim_{|\delta(0)| \rightarrow 0} \frac{1}{t} \ln \frac{|\delta(t)|}{|\delta(0)|} \quad (21)$$

where $\delta(0)$ is a perturbation in the initial condition, namely $\mathbf{x}(0) \rightarrow \mathbf{x}'(0) = \mathbf{x}(0) + \delta(0)$, and $\delta(t) = S^t \mathbf{x}'(0) - S^t \mathbf{x}(0)$ measures the separation between trajectories.

The Lyapunov exponent allows to quantitatively measure the degree of instability of a system's evolution, introducing the precise notion of chaos:

Definition (Chaos). A dynamical system is called chaotic if its first Lyapunov exponent is positive.

We note in passing that integrable systems have a null Lyapunov exponent and initial perturbations in the trajectories grow as polynomials.

Inspired by the discussion about the FPU problem, one is tempted to regard chaos as a necessary ingredient for the validity of statistical mechanics. Instead, we present here two examples, namely the FPU system itself and a model of coupled rotators, to show that chaos is neither sufficient nor necessary to ergodic behavior.

In the FPU system, at fixed value of the perturbation parameter ϵ , the Lyapunov exponent is positive whatever be the value of the energy density ξ . However, one observes thermalization only when the energy density is larger than a threshold value $\xi > \xi_c$. This would suggest that chaos, despite not being sufficient, is at least necessary to ergodicity.

Conversely, a ready counter-example is provided by the XY model, where a non-chaotic regime is accompanied by ergodicity breakdown. The model consists of a chain of N coupled rotors of angular momentum m and orientations $\theta_n \in [0, 2\pi)$:

$$H = \sum_{n=1}^N \left[\frac{p^2}{2m} + \epsilon (1 - \cos(\theta_n - \theta_{n-1})) \right]. \quad (22)$$

There are two opposite limits when the system becomes integrable: at very small energy density $\xi \rightarrow 0$, when the interaction is approximately harmonic, and at very large energy density $\xi \rightarrow \infty$, when the rotors are almost independent. The Lyapunov exponent λ approaches zero in these two limits, but has a maximum in between. Notwithstanding the presence of chaos for sufficiently large ξ , it was observed [16,17] that the ensemble averaged values of the specific heat C_v does not match the results of numerical simulations of (22), i.e. with the time average of the fluctuations of energy in subsystems. On the contrary in the other integrable limit (i.e. small energy), although the system is not chaotic (or very weakly chaotic), the specific heat C_v computed with the time average of the fluctuations of energy in subsystems, is in perfect agreement with the results of the canonical ensemble.

The different behavior of C_v in the two near-integrable regimes of low and high temperature can be understood as follows. For the FPU system and for the low temperature rotators the “natural” variables are the normal modes, which, even in a statistical analysis, are able to show regular behavior and where the energy of the system is resident. However, even if the normal modes are almost decoupled, when observing the energy of a subsystem, identified by some set of “local” variables $\{q_j, p_j\}$, non-negligible fluctuations of the “local” energy can be seen. On the other hand, for the chain of rotators at large energy the normal modes, i.e. the carriers of the energy, are the “local” variables $\{q_j, p_j\}$ themselves, and therefore the fluctuations of the local energy are strongly depressed, as is the exchange of energy among the subsystems.

5. Mixing

If a deterministic dynamical system is described by the flow $\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x})$, the associated probability density evolves in time according to the Liouville equation:

$$\partial_t \rho(\mathbf{x}, t) + \mathbf{F}(\mathbf{x}) \cdot \partial_{\mathbf{x}} \rho(\mathbf{x}, t) = 0. \quad (23)$$

The invariant density, if it exists, is the density $\rho(\mathbf{x})$ that satisfies the equation $\mathbf{F} \cdot \partial_{\mathbf{x}} \rho(\mathbf{x}) = 0$. As we have seen, if the dynamical behavior is periodic, the system keeps memory of the initial condition $\rho(\mathbf{x}, 0)$ and no relaxation to the invariant density takes place. The sufficient condition that ensures the invariant density to be eventually reached is mixing [2]:

Definition (Mixing). A dynamical system (Ω, S^t, μ) is called mixing if, for all measurable sets $D, E \subset \Omega$, one has

$$\lim_{t \rightarrow \infty} \mu(D \cap S^{-t}E) = \mu(D)\mu(E). \quad (24)$$

In words, the fraction of points starting from D and ending up in E after a long time is the product of the measures of D and E , whatever their position in Ω . A consequence of relation (24) is that generic functions of \mathbf{x} become uncorrelated in the long time limit:

$$\lim_{t \rightarrow \infty} \langle A(\mathbf{x}(t))B(\mathbf{x}(0)) \rangle = \langle A(\mathbf{x}) \rangle \langle B(\mathbf{x}) \rangle, \quad (25)$$

where the average is on the invariant measure. Of course, the mixing condition is stronger than ergodicity, i.e. mixing systems are ergodic of necessity [2].

6. Chaos and coarse-graining

In this section we discuss more thoroughly the role of chaos in dynamical system and in particular its repercussions on mesoscopic level of descriptions, i.e. when coarse-graining approximations are performed. This is of extreme importance for very many physical cases, where microscopic dynamics are in general not amenable to exact analytical studies and experimental observations due, respectively, to the inherent complexity and the finite resolution of the measurements. With this aim, we introduce, via an information theory approach, and exploit the concept of entropy of a dynamics system, trying to address the following questions:

- What informations about the system can entropy provide and how is it affected by different coarse-graining approximations?
- How much do we know of the coarse-grained system from the microscopic Lyapunov exponent? Are there general results in this direction?

These questions are tightly linked, but for clarity will be discussed separately.

6.1. Information theory entropy

Consider a set of symbols $\{s_1, \dots, s_T\}$ as the outcome of a certain process, e.g. integers belonging to the set $s_i \in \{1, \dots, M\}$ emitted by a source. In order to measure the information content of the N -word ensemble one associates to the N -word $W_N = (s_1, \dots, s_N)$ the block entropy:

Definition (Block Entropy). Given an ensemble of words $\{W_N\}$, the block entropy is:

$$H_N \equiv - \sum_{\{W_N\}} P(W_N) \ln P(W_N), \quad (26)$$

where $P(W_N) = P(s_1, \dots, s_N)$ is the occurrence probability of the word W_N .

In the following the occurrence probability is assumed stationary. The block entropy allows one to define a central quantity linking information theorem and statistical mechanics, namely, the Shannon entropy [18]:

Definition (Shannon Entropy). The Shannon entropy is defined as the entropy per symbol:

$$h_{\text{Sh}} \equiv \lim_{N \rightarrow \infty} \frac{H_N}{N} = \lim_{N \rightarrow \infty} (H_N - H_{N-1}). \quad (27)$$

The Shannon entropy quantifies the asymptotic uncertainty about the further emission of a symbol s in a very long sequence. The connection between the Shannon entropy and the thermodynamic entropy is given by the Shannon–McMillan theorem [5]:

Theorem (Shannon–McMillan). The ensemble of N -words can be divided into two classes, $\Omega_1(N)$ and $\Omega_0(N)$, such that, when $N \rightarrow \infty$:

$$\sum_{W_N \in \Omega_1(N)} P(W_N) \longrightarrow 1, \quad \sum_{C_N \in \Omega_0(N)} P(C_N) \longrightarrow 0,$$

and all the words $W_N \in \Omega_1(N)$ have the same probability $P(W_N) \sim \exp(-Nh_{\text{Sh}})$.

Put in other words, the theorem states that the occurrence probability $P(W_N)$ assigned to a (very long) sequence will be close to $\exp(-Nh_{\text{Sh}})$ and independent of the specific sequence. Therefore, the Shannon entropy counts the number of effectively observed sequences $\mathcal{N}(\Omega_1(N))$, i.e. $Nh_{\text{Sh}} \sim \ln \mathcal{N}(\Omega_1(N))$, exactly as the thermodynamic entropy, $S = k_B \ln W$, counts the number of microscopic configurations W corresponding to a macroscopic state of a physical system.

6.2. Entropy in coarse-grained dynamical systems

Let us now apply the notions introduced in the previous paragraph to a deterministic dynamical system. First, we perform a partition \mathcal{A} of the phase space Ω , with $\{s\}_{\mathcal{A}}$ numbering the partition cells, and define a sampling time τ . Then, we construct the word $W_N = (s(i), \dots, s(i + N - 1))$, where $s(i)$ labels the cell visited by the trajectory $\mathbf{x}(t)$ at time $i\tau$. If the system is ergodic, observing the frequencies of the words W_N , we can construct the block entropies $H_N(\mathcal{A})$ and the Shannon entropies $h_{\text{Sh}}(\mathcal{A})$ as defined, respectively, in (26) and (27). In order to get a quantity independent of the chosen partition one introduces the Kolmogorov–Sinai (K–S) entropy [19,20]:

Definition (Kolmogorov–Sinai Entropy). Given a set of partitions $\{\mathcal{A}\}$ of the phase space of the dynamical system (Ω, S^t, μ) , the Kolmogorov–Sinai entropy is defined as:

$$h_{\text{KS}} = \sup_{\mathcal{A}} h_{\text{Sh}}(\mathcal{A}). \quad (28)$$

Thanks to the Shannon–McMillan theorem, a precise physical meaning can be assigned to h_{KS} . Namely, called $N(\epsilon, t)$ the number of sizeably probable trajectories originating from a cell of edge $\epsilon \rightarrow 0$, the K–S entropy expresses their exponential growth rate in the long-time limit:

$$h_{\text{KS}} t \sim \ln N(\epsilon, t). \quad (29)$$

There is an important relation between h_{KS} and the Lyapunov exponent. Indeed, the K–S entropy of typical Hamiltonian systems can be expressed in terms of the Lyapunov exponents [21]:

$$h_{\text{KS}} = \sum_{\lambda_n > 0} \lambda_n. \quad (30)$$

In very low-dimensional chaotic systems, where only one Lyapunov exponent is generally positive, the K–S entropy is simply $h_{\text{KS}} = \lambda_1$.

The Kolmogorov–Sinai entropy of a system gives a measure of the amount of information per unit of time needed to reproduce a trajectory with arbitrary precision [[6], sec 2.3.4]. Nevertheless, in reality finite resolution makes impossible to compute h_{KS} . Therefore, we have to content ourselves with measuring the amount of information needed to reproduce trajectories with finite accuracy ϵ . To this end, one introduces partitions \mathcal{A}_ϵ based on cells of size ϵ that define a Shannon entropy $h_{Sh}(\mathcal{A}_\epsilon, \tau)$, where the τ dependence indicates the fine time resolution. Making the latter quantity independent of the partition, one introduces the ϵ -entropy [22]:

Definition (ϵ -entropy). The ϵ -entropy is the infimum over all partitions \mathcal{A}_ϵ whose cell diameter is smaller than ϵ :

$$h(\epsilon, \tau) = \inf_{\mathcal{A}_\epsilon: \text{diam}(\mathcal{A}_\epsilon) < \epsilon} h_{Sh}(\mathcal{A}_\epsilon, \tau). \quad (31)$$

It is easy to convince oneself that in the limit of infinite accuracy, i.e. when $\epsilon \rightarrow 0$, the K-S entropy is recovered for deterministic systems:

$$h_{KS} = \lim_{\epsilon \rightarrow 0} h(\epsilon). \quad (32)$$

Furthermore the ϵ -entropy is also a proper definition of entropy in stochastic systems where the Kolmogorov–Sinai entropy is ill defined due to the absence of the supremum required by definition (28) [22].

An important result for the ϵ -entropy in stochastic dynamical system is given by the theorem [23]:

Theorem (Kolmogorov). Given a Gaussian stochastic process $x(t)$ whose mean square displacement behaves as:

$$\langle (x(t + \Delta t) - x(t))^2 \rangle \propto \Delta t^{2\alpha} \quad (33)$$

with $0 \leq \alpha < 1$. The ϵ -entropy is:

$$\lim_{\tau \rightarrow 0} h(\epsilon, \tau) \propto \epsilon^{-\frac{1}{\alpha}}. \quad (34)$$

6.3. Chaos and diffusion

We are now in the position to discuss the questions we asked at the beginning of this section. As first example consider the following discrete-time evolution law [6,24]:

$$x_{t+1} = [x_t] + f(x_t - [x_t]) \quad (35)$$

where $[x]$ means the integer part of x , and $f(y)$ is defined as:

$$f(y) = \begin{cases} (2 + \alpha)y & \text{if } y \in [0, 1/2) \\ (2 + \alpha)y - (1 + \alpha) & \text{if } y \in [1/2, 1] \end{cases}$$

where $\alpha > 0$. The maximum Lyapunov exponent is computed as:

$$\lambda_1 = \ln \left| \frac{df}{dy} \right| = \ln |2 + \alpha| > 0, \quad (36)$$

which shows that the map is chaotic for every value of α . In addition, for long observation times the map (35) displays a diffusive behavior [25] characterized by the diffusion coefficient D :

$$\langle (x_t - x_0)^2 \rangle \approx 2Dt, \quad (37)$$

where $\langle \cdot \rangle$ denotes an average over the initial conditions. In view of the relations (32) and (34), one obtains the following behavior of the ϵ -entropy:

$$h(\epsilon) \sim h_{KS} = \lambda_1 \quad \text{if } \epsilon \ll 1, \quad (38)$$

$$h(\epsilon) \sim \frac{D}{\epsilon^2} \quad \text{if } \epsilon \gg 1. \quad (39)$$

The latter relations show that:

- when $\epsilon \ll 1$ the ϵ -entropy reduces to the Kolmogorov–Sinai one. Since the first Lyapunov exponent determines the value of the entropy, the dynamics is characterized by the fastest time scale and the microscopic details.
- for $\epsilon \gg 1$ the last relation suggests the existence of a de-correlation time so that, at large scales, the microscopic details become unimportant.

At first glance, one may be tempted to think that deterministic diffusion can appear with positive Lyapunov exponents only. For example, think of a free particle moving through hard obstacles. If the obstacles are convex and positioned on a lattice (Lorentz–Sinai billiard), the Lyapunov exponent is positive and the long-time behavior is diffusive [26]. Conversely, if the obstacles are randomly distributed polygons (wind-tree Ehrenfest model), the Lyapunov exponent is zero, but the long-time behavior is still diffusive. Therefore, one has to conclude that chaotic behavior does not imply the existence of the Arnold-diffusion, nor vice versa. We can understand that the Lyapunov exponent discussed so far is given by the microscopic details of the dynamics and thus is unable to characterize the macroscopic behavior.

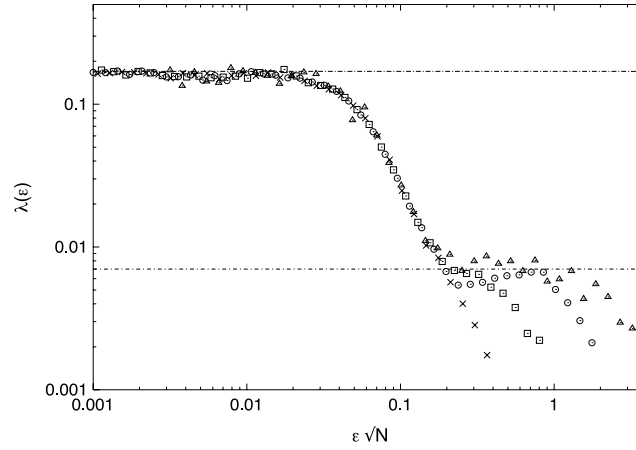


Fig. 2. The finite size Lyapunov exponent $\lambda(\epsilon)$ for the map (40) with $c = 0.3$, $a = 1.7$, $N = 10^4, 10^5, 10^6, 10^7$, as function of the coarse-graining scale ϵ/\sqrt{N} . The Lyapunov exponent for the microscopic scale ($\epsilon \rightarrow 0$) reaches the plateau-value λ_1 that is larger than the Lyapunov exponent for the macroscopic scale λ_M . This is a “universal” property that does not depend on the specific map. The macroscopic Lyapunov exponent saturates at about $\epsilon \approx 1/\sqrt{N}$.

Up to this point we have seen that, in low dimensional systems:

- we can associate an entropy to every chaotic system. Its value depends on the coarse-graining approximation.
- when the coarse-graining scale is at “atomic” scales, the entropy is given by the first Lyapunov exponent.
- when the coarse-graining scale is coarser, the entropy of a chaotic system is given by an effective “diffusion” coefficient. But we have no information about the Lyapunov exponents of the macroscopic observables.

6.4. Lyapunov exponent and coarse-graining

We discuss now the relation between the Lyapunov exponent of a microscopic description of a dynamical system, and the Lyapunov exponent of the coarse-grained one. As an example we discuss the globally coupled map of N interacting particles:

$$x_n(t+1) = (1-c)f(x_n(t)) + \frac{c}{N} \sum_{n' \neq n}^N g_c(x_{n'}(t)), \quad (40)$$

with $g_c(x) = (1/2 - |x - 1/2|)$. The above system can be considered as a picture of a gas of N interacting particles. A macroscopic observable associated to the microscopic dynamics (40) can be the center of mass position:

$$M(t) = \frac{1}{N} \sum_n x_n = \langle x_n \rangle + o\left(\frac{1}{\sqrt{N}}\right). \quad (41)$$

We call λ_1 and λ_M the first Lyapunov exponents of the observables $x_n(t)$ and $M(t)$, respectively. The behavior of the Lyapunov exponent for different coarse-graining approximations was studied numerically with the so called finite size Lyapunov exponent $\lambda(\epsilon)$ (which is based on the same idea of the ϵ entropy [27,28]) yielding the following limit behaviors:

$$\lambda(\epsilon) \simeq \lambda_M \leq \lambda_1 \quad \text{when } \epsilon \ll \frac{1}{\sqrt{N}} \quad (42)$$

$$\lambda(\epsilon) \simeq \lambda_1 \quad \text{when } \epsilon \gg \frac{1}{\sqrt{N}}. \quad (43)$$

The behavior of $\lambda(\epsilon)$ has a characteristic coarse-graining threshold $\epsilon \sim \frac{1}{\sqrt{N}}$ separating the microscopic Lyapunov exponent (42) from the macroscopic one (43). To be more precise, for the value of $\lambda(\epsilon)$ we observe two plateaus: $\lambda(\epsilon < \epsilon_1) \approx \lambda_1$ and $\lambda(\epsilon > \epsilon_2) \approx \lambda_M$. The values of ϵ_1 and ϵ_2 are of the order of $1/\sqrt{N}$ and generically $\lambda_1 \geq \lambda_M$ (see Fig. 2).

7. Some final general remarks

Let us conclude with some remarks on ergodicity and chaos with respect to the foundation of statistical mechanics. First we note that the ergodic approach can be seen as a natural way to introduce probabilistic concepts in a deterministic context. It seems to us that the ergodic theory provides support for the frequentistic interpretation of probability in the foundation of statistical mechanics. The other way (which is not in disagreement with the point of view of Boltzmann) to introduce probability is to assume an amount of uncertainty in the initial conditions. This approach is due to Maxwell who considers

that there are *a great many systems the properties of which are the same, and that each of these is set in motion with a different set of values for the coordinates and momenta*. Since one is forced to deal with a unique system (although with many degrees of freedom) it seems natural to assume that the purpose of statistical mechanics, for equilibrium phenomena, is to calculate time averages according to the temporal evolution of the system.

Therefore the ensemble theory should be seen only as a practical mathematical tool and the ergodic theory (or a “weak” version, such as that of Khinchin and Mazur and van der Linden) is an unavoidable step. Of course there is no complete consensus on this; for example Jaynes’s opposite opinion is that ergodicity is simply not relevant for the Gibbs method.

The ergodicity is, at the same time, an extremely demanding property (i.e. the time and phase averages must be equal for almost all the initial conditions), and not very conclusive at a physical level (because of the average over an infinite time). On the other hand, in the quasi-integrable limit the analytical results (KAM theorem) give only qualitative indications and do not allow for quantitative aspects. Therefore it is not possible to avoid detailed numerical investigations. Let us note that in the numerical computations based on the molecular dynamics one basically assumes that ergodicity somehow holds (although not in a strict mathematical sense) for the physically relevant observables.

There are also opposing answers to the question of whether the systems which are described by statistical mechanics must have a large number of degrees of freedom, and it is possible to find eminent scientists with opposite opinions. For instance according to Grad *the single feature which distinguishes statistical mechanics is the large number of degrees of freedom*. One can read rather similar sentences in the well known textbook of Landau and Lifshitz. In contrast Gibbs believed that *the laws of statistical mechanics apply to conservative systems of any number of degrees of freedom, and are exact*. Extended simulations on high-dimensional Hamiltonian systems show in a clear way that chaos is not necessarily a fundamental ingredient for the validity of equilibrium statistical mechanics: the naïve idea that chaos implies good statistical properties is inconsistent. Indeed sometimes, even in the absence of chaos (in agreement with Khinchin’s ideas), one can have good agreement between the time averages and their values predicted by equilibrium statistical mechanics.

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Inflow rate, a time-symmetric observable obeying fluctuation relations

Marco Baiesi^{1,2,*} and Gianmaria Falasco^{3,†}

¹*Department of Physics and Astronomy, University of Padova, Via Marzolo 8, I-35131 Padova, Italy*

²*INFN, Sezione di Padova, Via Marzolo 8, I-35131 Padova, Italy*

³*Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, D-04009 Leipzig, Germany*

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While entropy changes are the usual subject of fluctuation theorems, we seek fluctuation relations involving time-symmetric quantities, namely observables that do not change sign if the trajectories are observed backward in time. We find detailed and integral fluctuation relations for the (time-integrated) difference between *entrance rate* and escape rate in mesoscopic jump systems. Such *inflow rate*, which is even under time reversal, represents the discrete-state equivalent of the phase-space contraction rate. Indeed, it becomes minus the divergence of forces in the continuum limit to overdamped diffusion. This establishes a formal connection between reversible deterministic systems and irreversible stochastic ones, confirming that fluctuation theorems are largely independent of the details of the underlying dynamics.

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I. INTRODUCTION

The past two decades were characterized by the discussion of fluctuation relations (FRs), or fluctuation theorems, valid for systems arbitrarily far from equilibrium conditions [1–21] (the literature on FRs is vast, see more references in the reviews in Refs. [22–25]). Initially the focus was on deterministic dynamical systems, where Lyapunov exponents were found to play a fundamental role [1–4]. Although quantities as the phase-space contraction rate (minus sum of all Lyapunov exponents) are related to the entropy production [23], this concept acquires a more immediate physical interpretation in terms of heat flows when stochastic systems are considered [6–12, 18–21, 25]. For this reason, and because of the relevance for modern technological applications, nowadays it is more frequent to discuss FRs for stochastic dynamics.

The production of entropy, $S(\omega)$, being related to fluxes of heat, matter, etc., changes sign if one goes through the trajectory ω backward in time. By now it is essentially understood that any FR under examination involves a form of entropy production and that it yields a measure of the statistical asymmetry of physical processes in time. For example, the integral FR $\langle e^{-S} \rangle = 1$ ($\langle \dots \rangle$ denotes a statistical average) and the convexity of the exponential function provide a statistical mechanical derivation of the second law of thermodynamics, $\langle S \rangle \geq 0$. Such asymmetry in time exists already at the level of trajectories. Entropy production is the physical quantity that always determines the time-antisymmetric sector of path probabilities [12, 25],

$$P(\omega) \sim e^{-A(\omega)} \sim e^{\frac{1}{2}[S(\omega) - K(\omega)]}, \quad (1)$$

which is generally written as an exponential of some functional \mathcal{A} . This includes also a time-symmetric (TS) component $K(\omega)$. Yet such a quantity is completely irrelevant in the standard procedure used to prove FRs, in which one compares path weights (1) with those of trajectories reversed in time.

However, it is important to sharpen our understating of the meaning and the statistics of TS quantities, since it is becoming clear that they are necessary in the formulation of nonequilibrium statistical mechanics. A TS quantity that was recognized as a major player in characterizing the evolution of glassy systems is dynamical activity [26–33], which is just the number of jumps (or changes of state) that take place during a trajectory, regardless of their direction. Moreover, in the context of linear response theory, one finds fluctuation-dissipation relations where $K(\omega)$ complement the entropy production in determining the response of systems far from equilibrium [34–38]. Mostly these TS observables were continued to be called dynamical activity, although sometimes also the names “traffic” [39] or “frenesy” [36] were adopted. There are few examples of fluctuation symmetries for TS quantities [28, 33]. Therefore, to better understand the physics of nonequilibrium systems, there remains the interest of going deeper in this direction and find more variants of FRs for TS observables.

In this paper we briefly introduce some FRs for TS quantities. In discrete jump processes we study the *inflow rate* in a state, expressed as a properly defined entrance rate minus the standard escape rate. The derivation of FRs is based on an artificial “auxiliary” dynamics. A similar idea was recently put forward [21] to define the path-space probability of trajectories reversed in time when some transitions are only one way (i.e., their reverse transition does not exist). With such an approach one may draw a generalized FR [21]. By taking this method to the extreme, we will define the auxiliary dynamics as that taking place when all jump rates are flipped. It is a simple mathematical choice that leads to specific FRs. The probability of the auxiliary dynamics, appearing in such FRs, can be traced out and one is left with integral FRs, valid for the normal dynamics and in terms of sound physical quantities.

When we perform the limit to overdamped diffusive dynamics, we make contact with the approach by Maes and van Wieren [28]: The auxiliary dynamics here corresponds to flipping the force signs and the inflow rate becomes minus the divergence of the forces, which is the phase-space contraction rate of the associated noiseless dynamics. In our case the contraction rate is even under time reversal,

*baiesi@pd.infn.it

†falasco@itp.uni-leipzig.de

differently from the case of reversible deterministic dynamical systems. Nevertheless, an integral fluctuation for this quantity is derived. Note that the contraction rate can be found, for conservative forces, within the definition of the so-called effective potential, which is used in computations of reaction pathways [40] and in evaluations of the system activity [41,42].

II. JUMP PROCESS

We consider a system with discrete states $\{C\}$ whose probabilities ρ_t evolve according to the master equation

$$\partial_t \rho_t(C) = \sum_{C' \neq C} [\rho_t(C')k(C' \rightarrow C) - \rho_t(C)k(C \rightarrow C')], \quad (2)$$

where $k(C \rightarrow C')$ is the transition rate from configuration C to C' . The last term in the master equation contains the probability $\rho_t(C)$ times the escape rate from C ,

$$\lambda(C) \equiv \sum_{C' \neq C} k(C \rightarrow C'). \quad (3)$$

Here, next to this concept, we find it useful to define the entrance rate $\varepsilon(C)$ as the sum of transition rates from C' to C ,

$$\varepsilon(C) \equiv \sum_{C' \neq C} k(C' \rightarrow C). \quad (4)$$

In physics often one considers transition rates obeying local detailed balance [43] at temperature $T = 1/\beta$,

$$k(C \rightarrow C') \sim \exp\left[\frac{\beta}{2}\mathcal{W}(C \rightarrow C')\right], \quad (5)$$

where $\mathcal{W}(C \rightarrow C')$ is the work done by the system on its environment (a heat bath in equilibrium). The term $\beta\mathcal{W}(C \rightarrow C')$ thus represents the increase of entropy in the environment associated to the jump $C \rightarrow C'$ in the system.

A trajectory from time $t_0 = 0$ to time t is the time-ordered sequence $\omega \equiv \{C(s)|0 \leq s \leq t\} = \{C_0 = C(0), C_1, C_2, \dots, C_n = C(t)\}$ with n jumps $C_{i-1} \rightarrow C_i$ taking place at times t_i . For a system with initial density $\rho_0(C)$, the probability to observe a trajectory ω is proportional to

$$\begin{aligned} P(\omega) &\sim \rho_0(C_0)e^{-\lambda(C_n)(t-t_n)} \prod_{i=0}^{n-1} k(C_i \rightarrow C_{i+1})e^{-\lambda(C_i)(t_{i+1}-t_i)} \\ &\sim \rho_0(C_0)e^{-\int_0^t ds \lambda(C(s))} \prod_{i=0}^{n-1} k(C_i \rightarrow C_{i+1}) \end{aligned} \quad (6)$$

(we are omitting a time-discretization prefactor that is common to all trajectories with the same number of jumps [44]). The standard FR of the entropy production is obtained already at the level of single trajectories by comparing $P(\omega)$ with the probability of the path reversed in time, which we obtain by applying an involution θ that reverses the order of times ($\theta\omega \equiv \{C(t-s)|0 \leq s \leq t\}$, i.e., the initial time of $\theta\omega$ is what it was the final time for ω , etc.). Thus,

$$\frac{P(\omega)}{P(\theta\omega)} = e^{S_{\text{tot}}(\omega)}, \quad (7)$$

with

$$\begin{aligned} S_{\text{tot}}(\omega) &= -\ln \rho_t(C_n) + \ln \rho_0(C_0) + \beta \sum_{i=0}^{n-1} \mathcal{W}(C_i \rightarrow C_{i+1}) \\ &= -\ln \rho_t(C_n) + \ln \rho_0(C_0) + S(\omega), \end{aligned} \quad (8)$$

where $S(\omega)$ is the entropy increase in the heat bath. From (7) one readily observes that an increase of the entropy in the bath is associated with processes more likely to take place in the normal direction of time, because typically $\frac{P(\omega)}{P(\theta\omega)} > 1$ in this case (excluding effects from the boundary terms). Note that by construction this equation picks up the time-antisymmetric portion of the path measures and completely forgets about the integral of escape rates.

To obtain a new form of FR we do not simply consider time reversal but we rather define an auxiliary dynamics where all rates are replaced by the rates of the inverse transitions,

$$k^*(C \rightarrow C') \equiv k(C' \rightarrow C), \quad (9)$$

so the ‘‘auxiliary’’ escape rates correspond to the entrance rates of the normal dynamics,

$$\lambda^*(C) \equiv \sum_{C' \neq C} k^*(C \rightarrow C') = \varepsilon(C). \quad (10)$$

Note that other choices for ‘‘adjoint dynamics’’ have already been discussed [15–17]. However, those are useful to single out specific entropy production terms only.

The state density ρ^* with the auxiliary dynamics is chosen to be the same ρ we have with the normal dynamics. Thus, the path probability under the auxiliary dynamics is

$$\begin{aligned} P^*(\omega) &\sim \rho_0^*(C_0)e^{-\int_0^t dt' \lambda^*(t')} \prod_{i=0}^{n-1} k^*(C_i \rightarrow C_{i+1}) \\ &\sim \rho_0(C_0)e^{-\int_0^t dt' \varepsilon(t')} \prod_{i=0}^{n-1} k(C_{i+1} \rightarrow C_i), \end{aligned} \quad (11)$$

while for the corresponding time-reversed path it reads

$$P^*(\theta\omega) \sim \rho_t(C_n)e^{-\int_0^t dt' \varepsilon(t')} \prod_{i=0}^{n-1} k(C_i \rightarrow C_{i+1}). \quad (12)$$

The initial densities of $P^*(\omega)$ and $P^*(\theta\omega)$ are taken to be the initial and final densities of the physical trajectory, respectively, ρ_0 and ρ_t . Any other choice is equally allowed, though (see Sec. IV).

It is clear that the ratio of the path measure (11) or (12) with (6) now yields the exponential of a novel path-dependent term

$$\begin{aligned} Y(\omega) &= \int_0^t dt' [\varepsilon(C(t')) - \lambda(C(t'))] \\ &\equiv \int_0^t dt' \mathcal{R}(C(t')), \end{aligned} \quad (13)$$

in which there plays a crucial role the instantaneous inflow rate, i.e., the imbalance between the entrance rate (4) and the escape rate (3),

$$\mathcal{R}(C) \equiv \varepsilon(C) - \lambda(C). \quad (14)$$

Specifically, the ratio of Eqs. (11) and (6) is

$$\frac{P^*(\omega)}{P(\omega)} = e^{-S(\omega)-Y(\omega)}, \quad (15)$$

while the ratio of Eqs. (12) and (6) is

$$\frac{P^*(\theta\omega)}{P(\omega)} = e^{\ln[\rho_t(C_n)/\rho_0(C_0)]-Y(\omega)}. \quad (16)$$

Using the fact that $P(\theta\omega)$ can be normalized to 1 [$\int \mathcal{D}\omega P^*(\theta\omega) = 1 = \langle 1 \rangle^*$] and the conversion of statistical averages $\langle \dots \rangle^* = \langle \dots P^*/P \rangle$, from (16) we obtain the integral FR

$$\langle e^{\ln[\rho_t(C_n)/\rho_0(C_0)]-Y(\omega)} \rangle = 1, \quad (17)$$

which becomes

$$\langle e^{-Y(\omega)} \rangle \rightarrow 1 \quad \text{for } t \rightarrow \infty \quad (18)$$

if the boundary contribution is irrelevant. This occurs, for instance, for $t \rightarrow \infty$ if the system has a finite number of states and is in a stationary regime, $\rho_t = \rho_0 \forall t$. The convexity of the exponential yields also the inequality $\langle Y(\omega) \rangle \geq 0$. A positive inflow rate is to be expected as it is easier on average to jump into the states with high ρ than into those with low ρ .

With a similar procedure but using (15) rather than (16) one obtains another FR

$$\langle e^{-Y(\omega)-S(\omega)} \rangle = 1, \quad (19)$$

where the entropy production S reappears next to Y . Note that (17) and (19) are valid also in transient conditions. An equation as (19) might be particularly interesting in transient regimes because it does not contain explicitly the initial and final density of states. Possibly it might help to study glassy systems, which are the paradigm of transient dynamics.

III. OVERDAMPED DIFFUSION

In order to identify the transformation of a diffusive dynamics equivalent to inverting the rates in a jump process we start from the generic Fokker-Planck equation [45] for the density $\rho_t(x)$,

$$\partial_t \rho_t(x) = -\partial_x(\mu F(x)\rho_t(x)) + D\partial_x^2 \rho_t(x), \quad (20)$$

where μ is a mobility, D is a diffusion constant, and $F(x)$ is a force. We discretize phase space in tiny units of size δ , so (20) turns into a master equation for configurations $\mathcal{C} = \dots, x - \delta, x, x + \delta, \dots$. With the standard assumption that the dynamics is performed by random walks with jumps to nearest neighbors $x \rightarrow y = x \pm \delta$, the discretization yields

$$\begin{aligned} \partial_t \rho_t(x) = & -\frac{\mu}{2\delta} [F(x+\delta)\rho_t(x+\delta) - F(x-\delta)\rho_t(x-\delta)] \\ & + \frac{D}{\delta^2} [\rho_t(x+\delta) + \rho_t(x-\delta) - 2\rho_t(x)], \end{aligned} \quad (21)$$

that can be rewritten as a master equation with transition rates

$$k(x \rightarrow y) = \begin{cases} \frac{D}{\delta^2} - \frac{\mu}{2\delta} F(x-\delta) & \text{if } y = x - \delta \\ \frac{D}{\delta^2} + \frac{\mu}{2\delta} F(x+\delta) & \text{if } y = x + \delta. \end{cases} \quad (22)$$

When we apply the transformation $k^*(x \rightarrow y) = k(y \rightarrow x)$ we obtain

$$k^*(x \rightarrow y) = \begin{cases} \frac{D}{\delta^2} + \frac{\mu}{2\delta} F(x) & \text{if } y = x - \delta \\ \frac{D}{\delta^2} - \frac{\mu}{2\delta} F(x) & \text{if } y = x + \delta. \end{cases} \quad (23)$$

The difference in the state where the forces are evaluated is of order $O(1)$ [46] and so vanishes when we go back to the continuous limit $\delta \rightarrow 0$ (D is assumed to be a constant). We conclude that changing the sign of F (or, alternatively, of μ) gives the transformed rates in terms of the original ones, namely $k_F^*(x \rightarrow y) = k_{-F}(x \rightarrow y)$. The path weight associated to (20), describing overdamped diffusive dynamics, is

$$P(\omega) \sim \rho_0[x(0)] \exp \left\{ -\int_0^t dt' \frac{[\dot{x}(t') - \mu F(t')]^2}{4D} - \frac{\mu}{2} \int_0^t dt' \partial_x F(t') \right\} \quad (24)$$

and it is straightforward to obtain the equivalent of (17) by applying time reversal together with the transformation $F^* = -F$ (or, equivalently, $\mu^* = -\mu$), which again gives the probability ratio

$$\frac{P^*(\theta\omega)}{P(\omega)} = \frac{\rho_t^*(x(t))}{\rho_0(x(0))} e^{-Y(\omega)} = e^{\ln[\rho_t(x(t))/\rho_0(x(0))]-Y(\omega)}, \quad (25)$$

where now the integral Y is

$$Y(\omega) = -\mu \int_0^t dt' \partial_x F(t'). \quad (26)$$

In Ref. [28] we find a previous example where one force was flipped to get a FR for TS quantities. Alternatively, we can get again

$$\frac{P^*(\omega)}{P(\omega)} = e^{-S(\omega)-Y(\omega)}, \quad (27)$$

where the entropy increase in the heat bath is here defined by

$$S(\omega) = \frac{\mu}{D} \int_0^t dt' F(t') \dot{x}(t'). \quad (28)$$

Therefore, we find Eqs. (17), (18), and (19) to be valid also in overdamped diffusing systems. Besides, from (25) one can as well derive detailed FRs that link the statistics of observables (odd under the joint inversion of time and forces) in two systems subject to opposite forces. Examples of practical interest are systems of noninteracting particles exposed to controllable external fields.

In more than one dimension and with $\mu = 1$, Eq. (26) reads

$$Y(\omega) = -\int_0^t dt' \partial_{x_i} F_i(\mathbf{x}(t')). \quad (29)$$

Einstein notation is used from here onward and the vector state is denoted as $\mathbf{x} \equiv \{x_i\}$. For overdamped stochastic systems the inflow rate is thus represented by a function with the structure of a divergence of forces,

$$\mathcal{R}(\mathbf{x}) = -\partial_{x_i} F_i(\mathbf{x}), \quad (30)$$

when all mobilities are equal to 1. This form has an analogous version in deterministic evolution, as discussed in the next section.

IV. ANALOGY WITH THE CONTRACTION RATE

Consider a dynamical systems composed of $i = 1, \dots, N$ degrees of freedom evolving according to deterministic equations

$$\dot{x}_i = F_i(\mathbf{x}). \quad (31)$$

In phase space the system is described by a density ρ which evolves according to the continuity equation, enforcing probability conservation:

$$\begin{aligned} \partial_t \rho(\mathbf{x}(t), t) &= -\partial_{x_i} [\dot{x}_i(t) \rho(\mathbf{x}(t), t)] \\ &= -\partial_{x_i} [F_i(\mathbf{x}(t)) \rho(\mathbf{x}(t), t)]. \end{aligned} \quad (32)$$

Rearranging the terms and introducing the Lagrangian derivative $d/dt \equiv \partial_t + \dot{x}_i \partial_{x_i}$ accounting for time variations along trajectories, we find

$$\frac{d}{dt} \ln \rho(\mathbf{x}(t), t) = -\partial_{x_i} F_i(\mathbf{x}(t)) \equiv \sigma(\mathbf{x}(t)). \quad (33)$$

In (33) we introduced the instantaneous contraction rate $\sigma(\mathbf{x})$, which measures the logarithmic rate of contraction of phase-space volumes [47]—it is identically zero in Hamiltonian systems and on average positive in dissipative ones [48]. This is exactly the quantity (30) for which we have derived a FR for the diffusive dynamics. Moreover, since the transformation used to find the FR in the discrete dynamics (see Sec. II) is analogous to that used to derive the FR in the diffusive dynamics, we conclude that the inflow rate $\mathcal{R}(\mathcal{C})$ is the equivalent of the contraction rate $\sigma(\mathbf{x})$.

There is indeed a procedure that illustrates this correspondence. In a discrete state system, we spread uniformly the occupation probability on the configuration \mathcal{C} and on its neighbors, i.e., those \mathcal{C}' such that $k(\mathcal{C} \rightarrow \mathcal{C}') \neq 0$. At $t = 0$ we thus have $\rho_0(\mathcal{C}) = \rho_0(\mathcal{C}') = 1/\mathcal{V}(\mathcal{C})$, where $\mathcal{V}(\mathcal{C})$ is the number, or “volume,” of the states centered around \mathcal{C} . Shortly after the preparation, the time derivative of the Boltzmann entropy associated to this locally flat density is expected to give the logarithmic variation of the inverse volume centered on \mathcal{C} . Therefore we have

$$\begin{aligned} \partial_t \ln \rho_t(\mathcal{C}(t))|_{t=0} &= \mathcal{V}(\mathcal{C}) \partial_t \rho_t(\mathcal{C})|_{t=0} \\ &= \mathcal{V}(\mathcal{C}) \sum_{\mathcal{C}'} [\rho_t(\mathcal{C}') k(\mathcal{C}' \rightarrow \mathcal{C}) - \rho_t(\mathcal{C}) k(\mathcal{C} \rightarrow \mathcal{C}')]|_{t=0} \\ &= \sum_{\mathcal{C}'} [k(\mathcal{C}' \rightarrow \mathcal{C}) - k(\mathcal{C} \rightarrow \mathcal{C}')] \\ &= \mathcal{R}(\mathcal{C}), \end{aligned} \quad (34)$$

which shows that the inflow rate measures the “volume” contraction rate.

The phase-space contraction rate is a key ingredient in the derivation of FRs for deterministic dynamics [22,23]. Hence we deem it interesting to strengthen the correspondence between thermostated deterministic systems (i.e., Hamiltonian systems with an added nonlinear friction term) and stochastic ones applying the ideas of Sec. II and Sec. III to underdamped diffusion, where the phase space does not simply reduce to the configuration space. For simplicity we consider two conjugated degrees of freedom only, $\mathbf{x} = \{q, mv\}$, exemplifying a

particle of mass m and friction coefficient γ moving in a force field F . The motion is described by the Langevin equations

$$\dot{q} = v, \quad m\dot{v} = -\gamma v + F(q) + \sqrt{2D_v} \xi, \quad (35)$$

where ξ is a standard Gaussian white noise with unit variance. Since the associated path weight is

$$\begin{aligned} P(\omega) &\sim \rho_0(x(0), v(0)) e^{\frac{\gamma}{2} t} \\ &\times \exp \left\{ -\int_0^t dt' \frac{[m\dot{v}(t') + \gamma v(t') - F(t')]^2}{4D_v} \right\}, \end{aligned} \quad (36)$$

the time-integrated contraction rate of the noiseless dynamics, $Y(\omega) = \gamma t$, is singled out by comparison with an auxiliary dynamics having negative friction coefficient, i.e., $\gamma^* = -\gamma$. Recalling that time reversal here implies $\theta v(t') = -v(t - t')$, the analogous of (25) for underdamped diffusion is

$$\frac{P^*(\theta\omega)}{P(\omega)} = e^{\ln[\rho_t^*(x(t), -v(t))/\rho_0(x(0), v(0))] - \gamma t}. \quad (37)$$

Essentially, this auxiliary dynamics emulates the time-reversal transformation of thermostated Hamiltonian systems. There [49], the friction coefficient γ is indeed replaced by the thermostat multiplier, that is, an odd function of the velocity v , and thus changes sign upon time inversion. Moreover, this auxiliary dynamics is equivalent to that used in Sec. III for underdamped diffusion, since $\gamma = 1/\mu$ and we have already noticed that flipping the forces is the same as changing the sign of the mobility.

Similarly to the deterministic case, Eqs. (25) and (37) can be turned into an integral FR for the dissipation function Ω [22],

$$\int_0^t dt' \Omega(\mathbf{x}(t')) \equiv \ln \rho_0(\mathbf{x}(0)) - \ln \rho_0(\mathbf{x}(t)) + \int_0^t dt' \sigma(\mathbf{x}(t')),$$

exploiting the freedom in choosing the initial density of the backward auxiliary trajectory. Specifically, taking $\rho_t^* = \rho_0$ in (25) we obtain the nonequilibrium partition identity, i.e., the integral version of the FR [14],

$$\left\langle \exp \left[-\int_0^t dt' \Omega(t') \right] \right\rangle = 1, \quad (38)$$

valid in overdamped diffusing systems for arbitrary initial densities and nonconservative forces. The same relation is obtained for underdamped diffusion from (37), provided that ρ_0 is independent of the sign of v , as it is, e.g., at equilibrium.

Finally, it is worth noting that the quantity (29) can also be related to the (finite-time) Lyapunov exponents Λ_i of the system. The latter are defined by considering the growth rates of k -dimensional volumes supported by k linearly independent perturbations $\delta \mathbf{x}^{(i)}$, with $1 \leq k \leq N$ [50]:

$$\text{Vol}_k(\{\delta \mathbf{x}^{(i)}(t)\}) \sim e^{\sum_{i=1}^k \Lambda_i t}. \quad (39)$$

The time evolution of such a perturbation $\delta \mathbf{x}$ in the initial condition of (31) is

$$\delta \dot{x}_i = F_i(\mathbf{x} + \delta \mathbf{x}) - F_i(\mathbf{x}) \approx (\partial_{x_j} F_i) \delta x_j \equiv (\nabla F)_{ij} \delta x_j, \quad (40)$$

which has the solution

$$\delta x_i(t) = \exp \left[\int_0^t \nabla F(t') dt' \right]_{ij} \delta x_j(0). \quad (41)$$

Therefore, using the formula relating the determinant to the trace, $\det(\exp A) = \exp(\text{Tr}A)$, the relative variation of the N volume is obtained as

$$\begin{aligned} \det \left[\frac{\delta x_i(t)}{\delta x_j(0)} \right] &= \exp \left[\int_0^t \partial_{x_i} F_i(t') dt' \right] \\ &= \exp \left[- \int_0^t \sigma(t') dt' \right], \end{aligned} \quad (42)$$

which gives the time-averaged contraction rate in terms of the negative sum of all Lyapunov exponents,

$$\frac{1}{t} \int_0^t \sigma(t') dt' = - \sum_{i=1}^N \Lambda_i. \quad (43)$$

If (31) is stochastic, as in the overdamped diffusion considered in the previous section, the Lyapunov exponents identify the separation rate of nearby trajectories subjected to the same noise realization, and Eqs. (25) and (27) are statements about the statistics of their spectrum. Note that Eqs. (27) and (25) can be restricted to quantities measured on subspaces of the full phase space using auxiliary dynamics where only some components of the forces are changed in sign. In particular, when $F_i^* = -F_i$ if $i = k$ and $F_i^* = F_i$ otherwise, we get, for example (no Einstein summation),

$$\left\langle \exp \left[- \frac{1}{D} \int_0^t dt' F_k(t') \dot{x}_k(t') + \int_0^t dt' \partial_{x_k} F_k(t') \right] \right\rangle = 1. \quad (44)$$

Since a k volume is obtained as the determinant of the $k \times k$ minor of $\delta x_i(t)/\delta x_j(0)$, Eq. (44) relates a single Lyapunov

exponent Λ_k ,

$$e^{t\Lambda_k} = \text{Vol}_k(t) - \text{Vol}_{k-1}(t) = \exp \left[\int_0^t dt' \partial_{x_k} F_k(t') \right], \quad (45)$$

to the entropy produced in the k direction.

V. CONCLUSIONS

We have introduced the concept of *inflow rate*. The fluctuations of its time integral are characterized by two fluctuation relations, one involving also boundary terms (density of states) and one involving the entropy production. In the continuum limit bringing jump systems to overdamped diffusion, the inflow rate becomes (minus) the divergence of forces, i.e., the phase-space contraction rate. This quantity in reversible deterministic dynamical systems is known to be odd under time reversal. However, in general the phase-space contraction rate can have any or no parity. In particular, in our case it results even under time reversal, due to the fact that the overdamped Langevin dynamics is not time reversible. Note that time reversibility is a condition commonly invoked in the derivations of FRs, hence it is sufficient, but it is known to be unnecessary [51–53].

We hope that these findings will be useful in developing nonequilibrium statistical mechanics—e.g., in deriving symmetry properties of response coefficients far from equilibrium, as much as standard FRs are employed around equilibrium to obtain the Onsager reciprocity relations [54]—for which by now it is clear that we need not only to have entropy flows under control but also to better understand the statistics of activities that have an even parity under time reversal.

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Exact symmetries in the velocity fluctuations of a hot Brownian swimmer

Gianmaria Falasco,^{1,*} Richard Pfaller,¹ Andreas P. Bregulla,² Frank Cichos,² and Klaus Kroy^{1,†}

¹*Institut für Theoretische Physik, Universität Leipzig, Postfach 100 920, D-04009 Leipzig, Germany*

²*Molecular Nanophotonics Group, Institute of Experimental Physics I, University of Leipzig, 04103 Leipzig, Germany*

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Symmetries constrain dynamics. We test this fundamental physical principle, experimentally and by molecular dynamics simulations, for a hot Janus swimmer operating far from thermal equilibrium. Our results establish scalar and vectorial steady-state fluctuation theorems and a thermodynamic uncertainty relation that link the fluctuating particle current to its entropy production at an effective temperature. A Markovian minimal model elucidates the underlying nonequilibrium physics.

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In 1905, Einstein pointed out that the velocity of a Brownian particle is not a well-defined observable, except for very short times [1]. A precise and detailed experimental confirmation of his early insight has only recently become possible [2,3]. Contrarily, to a self-propelled Brownian particle or “microswimmer”, a meaningful velocity can also be assigned in an intermediate asymptotic long-time regime, when its directed autonomous motion prevails over fluctuations and can thus be harnessed for potentially useful tasks [4–7]. The persistence of this motion is still limited by (possibly nonthermal) stochastic velocity fluctuations, though. As we demonstrate in the following, these fluctuations are not completely chaotic but encode a characteristic fingerprint of the underlying space-time symmetry, even far from thermal equilibrium.

We specifically consider a so-called hot (i.e., persistently heated) Brownian swimmer [7,8], in theory, experiment, and computer simulations. The swimmer is designed as a Janus sphere made of two hemispheres with unequal thermal and solvation properties, which excites phoretic surface flows upon heating. A variety of such phoretic self-propulsion mechanisms is commonly employed in the design of artificial microswimmers. They all rely on the creation of asymmetric gradients of a thermodynamic field (e.g., concentration of a solute [9], temperature [8]) in the solvent, which induces a systematic drift through classical interfacial phoretic processes [10]. Besides their biomimetic and practical relevance for promising applications in nanoscience, self-propelled particles are of fundamental interest as paradigmatic nonequilibrium systems. Their energy input is not due to fluxes at the boundary, as is often the case in macroscopically induced nonequilibrium states, but localized on the particle scale. And their self-propulsion is not due to a balance of external body forces with Stokes friction, as assumed in popular “dry-swimmer” models [11]. Instead, they are characterized by (hydrodynamic) long-range interactions very different from those found in driven colloids. In other words, microswimmers are not simply ordinary driven colloids in disguise. As a result, their collective behavior displays peculiar features, such as phases and phase transitions absent in sheared and sedimenting colloids, say [12,13]. But clear nonequilibrium

signatures are detected already on the single-particle level. Examples include non-Gaussian fluctuations [14], negative mobility for confined swimmers [15], and hot Brownian motion [16] for nonisothermal swimmers. Despite the possibility to experimentally track and manipulate single-particle trajectories [17], a less explored direction of research is the study of fluctuations of (thermodynamic) path observables, defined along trajectories, as in stochastic energetics [18,19]. In particular, one may wonder whether fluctuation theorems are valid for self-propelled particles [20].

Fluctuation theorems are symmetry relations holding for a wide class of nonequilibrium systems [21–26]. They quantify the irreversibility of nonequilibrium processes by their total entropy production S , saying that the probability $P(S)$ for positive S is exponentially larger than for negative S :

$$P(S) = P(-S)e^{S/k_B}. \quad (1)$$

For systems in contact with an equilibrium thermal reservoir, S is given by the dissipated heat over the bath temperature in the long-time limit. Such relations ultimately originate from the time-reversal invariance of the microscopic dynamics that is broken at the ensemble level by a nonconservative driving. More recently, additional fluctuation theorems were identified, which rely on the breaking of *spatial* symmetries of the underlying microscopic dynamics [27–29]. They relate the probabilities of vectorial observables pointing in different directions, such as the isometric currents \mathbf{J}_1 and \mathbf{J}_2 (currents of equal strength in different directions) excited by a homogeneous driving force \mathbf{f} in an isotropic system:

$$P(\mathbf{J}_1) = P(\mathbf{J}_2)e^{\mathbf{f} \cdot (\mathbf{J}_1 - \mathbf{J}_2)}. \quad (2)$$

For our hot Brownian swimmers (and other self-propelled particles), the validity of Eqs. (1) and (2) is *a priori* in doubt. First, the phoretic mechanism responsible for the entropy production is not an external deterministic driving, as usually assumed to derive Eqs. (1) and (2). In addition, due to the presence of strong and long-ranged thermodynamic gradients, the solvent is not an equilibrium bath. In the case of a swimmer generating a temperature gradient, the bath noise does not even possess a definite temperature but is generally characterized by a nontrivial noise temperature spectrum arising from hydrodynamic memory [30–32]. Hence, the thermal noise need not be Gaussian, thus altering in general the simple exponential form of the fluctuation relations (FRs) (unless the underlying large-deviation principle exceptionally

*falasco@itp.uni-leipzig.de

†klaus.kroy@itp.uni-leipzig.de

survives) [33–35]. Finally, Eq. (2) has been proved so far only for models that do not include inertia [36]. Despite all that, we now verify the fluctuation relations (1) and (2) relating the entropy production and the particle current for a hot Brownian swimmer both experimentally and numerically. A minimal analytical model helps to rationalize our findings.

The experimental system consists of a polystyrene bead of 500 nm radius, half-coated with a 50-nm-thick gold layer, in aqueous solution. It is narrowly confined between two glass plates coated with a nonionic surfactant (Pluronic) to prevent the particle from sticking. The sample is illuminated through a dark field condenser, and the scattered light is collected and imaged with a CCD camera. The particle's center of mass position \mathbf{r} and orientation \mathbf{n} (a unit vector along the symmetry axis from hot to cold) are recorded at an inverse frame rate of 5 ms. A 532 nm laser with incident intensity of $0.05 \text{ mW}/\mu\text{m}^2$ continuously heats the particle. The piezoposition employed for the spatial positioning of the sample is adjusted every 100 frames to keep the particle in the center of the Gaussian beam. The tangential surface gradient of the local temperature translates into a thermophoretic propulsion velocity $v_p \mathbf{n}$, stemming from the unbalanced particle-fluid interactions [10] plus thermo-osmotic contributions from the nearby glass covers [37].

A similar, but technically somewhat different realization of a hot swimmer was implemented numerically. We performed molecular dynamics simulations of 6×10^4 Lennard-Jones (LJ) atoms of mass m in a cubic box with periodic boundary conditions. The deterministic equations of motion are integrated by a velocity-Verlet algorithm. The 255 atoms belonging to the spherical swimmer were additionally bonded by a finitely extensible nonlinear elastic potential [38]. The standard LJ potential $4\epsilon[(\sigma/r)^{12} - c_{if}(\sigma/r)^6]$ was modified by introducing an effective wetting parameter c_{if} for the interactions between the fluid (f) and the atoms composing the two hemispheres ($i = a, b$) of the particle surface. They serve to mimic the asymmetric solvent heating by the gold cap and polystyrene body of the experimental particle, in an efficient way [39]. We used $c_{af} = 2$ and $c_{bf} = 1$ for all simulations reported in this Rapid Communication. In a typical simulation run, we first equilibrate the system in the Nosé-Hoover NVT ensemble at the prescribed temperature $T = 0.75\epsilon/k_B$ and with an average number density $\sim 0.8\sigma^{-3}$ of fluid particles. Subsequently, we switch off the global thermostat and only the atoms near the boundary of the simulation box are kept at the ambient temperature, whereas the atoms of one half of the particle surface are heated to a substantially elevated temperature $T_p = 1.5\epsilon/k_B$, by means of a standard velocity rescaling algorithm. After allowing the system to reach a steady state, we record time traces of the position \mathbf{r} and velocity \mathbf{V} of the particle's center of mass, as well as the particle orientation \mathbf{n} .

We start our analysis with the time-dependent diffusion coefficients parallel and perpendicular to \mathbf{n} ,

$$D_{\parallel}(t) = \frac{1}{2} \frac{d}{dt} \left\langle \left(\int_0^t d\tau \mathbf{V}(\tau) \cdot \mathbf{n}(\tau) \right)^2 \right\rangle, \quad (3)$$

$$D_{\perp}(t) = \frac{1}{4} \frac{d}{dt} \left\langle \left(\int_0^t d\tau \mathbf{V}(\tau) \cdot [\mathbf{1} - \mathbf{n}\mathbf{n}(\tau)] \right)^2 \right\rangle, \quad (4)$$

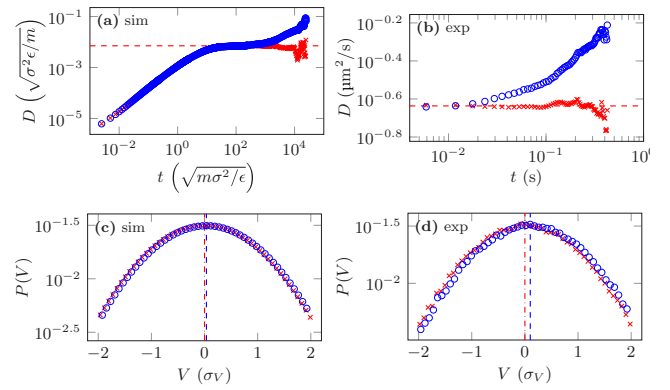


FIG. 1. Upper panel: longitudinal (\circ) and transverse (\times) time-dependent diffusivities D_{\parallel} and D_{\perp} in the particle frame, as measured in simulation (a) and experiment (b). Their common plateau gives the diffusion constant D , and the late-time asymptotics of $D_{\parallel}(t)$ the propulsion speed v_p . Lower panel: histograms of the corresponding short-time displacements.

where $\langle \dots \rangle$ denotes steady-state ensemble averaging. As seen from Fig. 1(a), the particle performs free diffusion in the perpendicular direction on times beyond the time scale τ_{st} ($\approx 10\sqrt{m\sigma^2/\epsilon}$ in the simulations) for velocity damping, given by the particle mass over the Stokes friction. This manifests itself as a plateau in $D_{\perp}(t)$, which can be used to read off the long-time translational diffusion constant as $D \equiv D_{\perp}(t \gg \tau_{st})$. Along the particle axis, the active drift $v_p = \langle \mathbf{n} \cdot \mathbf{V} \rangle$ (extracted from recorded trajectories by averaging over realizations and time) is superimposed as a ballistic component, so that $D_{\parallel}(t \gg \tau_{st}) \sim D + v_p^2 t$. The mixing of parallel and perpendicular dynamics in the laboratory frame randomizes the particle orientation $\mathbf{n}(t)$ at late times, giving rise to an enhanced apparent overall diffusion coefficient. Note that all mentioned diffusion and mobility coefficients are nonequilibrium transport coefficients, since (global) thermal equilibrium is broken. They subsume all parameters describing the solute, the solvent, and their mutual interactions, whose specific values are thus irrelevant at the mesoscopic level [39].

The data in Figs. 1(c) and 1(d) show that, despite the substantial thermal gradients attained in the simulations, the particle velocities parallel and perpendicular to \mathbf{n} are essentially Gaussian distributed. This demonstrates that the thermal agitation of the Janus particle can be attributed to a Gaussian noise. It also implies that, at least for the swimmer, the fluid can effectively be described as locally in thermal equilibrium, which is indeed a necessary assumption in standard theories of phoretic transport and nonisothermal Langevin descriptions.

From the above observations, the following picture for the physics underlying Eqs. (1) and (2) emerges. On average, the particle will be propelled along the axis \mathbf{n} , or more generally, such that $\mathbf{n} \cdot \dot{\mathbf{r}} > 0$. But on rare occasions, a fluctuation can displace it against the phoretic drift, such that $\mathbf{n} \cdot \dot{\mathbf{r}} < 0$. The two dissimilar situations correspond to energy dissipation to the fluid and energy extraction from it, respectively. While the first conforms with the expected thermodynamic behavior, the second represents an atypical transient fluctuation. Their relative rate is exactly quantified by Eq. (1).

To formalize this intuitive picture, we now propose a minimal model for the swimmer dynamics. By restricting our analysis to times $t \gg \tau_{st}$, the Brownian fluctuations are effectively diffusive, and the particle momentum and all hydrodynamic modes can be taken as fully relaxed. Long-time tails and any randomness in the swimming speed v_p , which may arise from the fluctuating fluid momentum and temperature, are discarded. On this level, the stochastic motion of the hot Janus particle can be represented by the active Brownian particle model [40], consisting of two isotropic Markov processes for its position and orientation vectors $\mathbf{r}(t)$ and $\mathbf{n}(t)$, with a superimposed constant drift along $\mathbf{n}(t)$. The corresponding overdamped Langevin equations read [41]

$$\dot{\mathbf{r}} = v_p \mathbf{n} + \sqrt{2D} \boldsymbol{\xi}_t, \quad (5)$$

$$\dot{\mathbf{n}} = \sqrt{2D_r} \boldsymbol{\xi}_r \times \mathbf{n}, \quad (6)$$

where $\boldsymbol{\xi}_t(t)$ and $\boldsymbol{\xi}_r(t)$ represent independent unbiased Gaussian white noise processes with unit variance. It allows us to explicitly construct the probability

$$P[\mathcal{X}] \propto \exp\left(-\frac{1}{4D} \int_0^t d\tau [\dot{\mathbf{r}}(\tau) - v_p \mathbf{n}(\tau)]^2\right) \quad (7)$$

associated with a path $\mathcal{X} \equiv \{\{\mathbf{r}(\tau), \mathbf{n}(\tau)\} : 0 \leq \tau \leq t\}$ (the ordered set of positions and orientations in the time interval $[0, t]$). The path weight given by Eq. (6) is omitted, because it is inessential, as is the initial configuration $\{\mathbf{r}(0), \mathbf{n}(0)\}$, because all allowed configurations are equiprobable for an unconfined particle in the steady state. The probability $P[\tilde{\mathcal{X}}]$ to observe the same event backwards in time is obtained from Eq. (7) by the time-reversal transformation $\tau \rightarrow t - \tau$. The two path weights are thus related by

$$P[\mathcal{X}] = P[\tilde{\mathcal{X}}] \exp\left(\frac{v_p}{D} \int_0^t d\tau \dot{\mathbf{r}}(\tau) \cdot \mathbf{n}(\tau)\right), \quad (8)$$

saying that a path \mathcal{X} resulting in a positive total displacement along \mathbf{n} is exponentially more probable than the reversed path $\tilde{\mathcal{X}}$ resulting in a negative displacement. To show that this leads to a measurable asymmetry, we define a time-averaged forward velocity [42]

$$j_{\parallel}[\mathcal{X}] \equiv \frac{1}{t} \int_0^t d\tau \dot{\mathbf{r}}(\tau) \cdot \mathbf{n}(\tau). \quad (9)$$

The probability that $j_{\parallel}[\mathcal{X}]$ attains a certain value, say J_{\parallel} , follows by multiplying both sides of Eq. (8) by $\delta(j_{\parallel} - J_{\parallel})$ and summing over all possible trajectories:

$$\sum_{\mathcal{X}} P[\mathcal{X}] \delta(j_{\parallel} - J_{\parallel}) = \sum_{\tilde{\mathcal{X}}} P[\tilde{\mathcal{X}}] e^{(v_p/D)t j_{\parallel}} \delta(j_{\parallel} - J_{\parallel}). \quad (10)$$

The left-hand side of Eq. (10) is, by definition, $P(J_{\parallel}) \equiv \text{Prob}(j_{\parallel}[\mathcal{X}] = J_{\parallel})$, while the right-hand side becomes

$$\sum_{\tilde{\mathcal{X}}} P[\tilde{\mathcal{X}}] e^{-(v_p/D)t j_{\parallel}} \delta(j_{\parallel} + J_{\parallel}) = P(-J_{\parallel}) e^{(v_p/D)t J_{\parallel}}$$

when we rewrite the sum over paths as sum over time-reversed paths and flip the sign of j_{\parallel} accordingly, since $j_{\parallel}[\tilde{\mathcal{X}}] =$

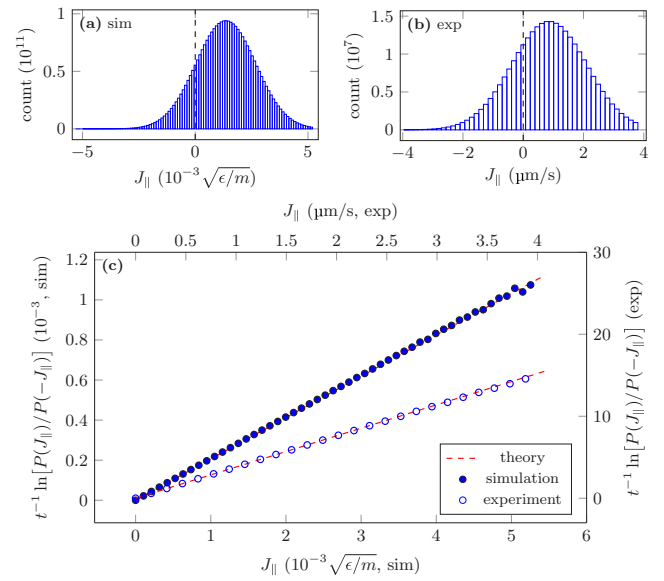


FIG. 2. Upper panel: histograms of the longitudinal particle current J_{\parallel} , Eq. (9), as measured in simulation (a) and experiment (b). Lower panel: test of the fluctuation theorem, Eq. (11), using these histograms as proxies for $P(J_{\parallel})$.

$-j_{\parallel}[\tilde{\mathcal{X}}]$. We thus obtain the fluctuation relation

$$\frac{1}{t} \ln \frac{P(J_{\parallel})}{P(-J_{\parallel})} = \frac{v_p}{D} J_{\parallel}. \quad (11)$$

It is valid for all observation times consistent with the Markov condition $t \gg \tau_{st}$. Differently from usual steady-state fluctuation relations, boundary terms corresponding to the density of states evaluated at times 0 and t are absent, being trivial constants. This enables us to verify the theory at relatively short times, which permits an efficient sampling of the negative tail of $P(J_{\parallel})$. Corresponding histograms constructed from the numerical and experimental data are shown in Figs. 2(a) and 2(b). The logarithmic ratios of statistically relevant opposite bins conform nicely with Eq. (11), as shown in Fig. 2(c).

The argument of the exponential in Eq. (8) may be cast into the explicit form of an entropy production by combining Eq. (8) with the generalized Sutherland-Einstein relation, $D = k_B T_{\text{eff}}/\zeta$. This amounts to replacing the nonisothermal solvent by a virtual isothermal bath at an effective temperature T_{eff} [31]. Thereupon, Eq. (8) takes the form of Eq. (1) with $P(S) \equiv \text{Prob}(s[\mathcal{X}] = S)$ and

$$s[\mathcal{X}] \equiv \frac{1}{T_{\text{eff}}} \int_0^t d\tau \dot{\mathbf{r}}(\tau) \cdot \mathbf{n}(\tau) v_p \zeta = \frac{j_{\parallel} v_p \zeta}{T_{\text{eff}}} t \quad (12)$$

the entropy produced by the ‘‘thermophoretic force’’ $n v_p \zeta$ (the phoretic velocity times the Stokes friction) acting along the path \mathcal{X} . Note that the appropriate temperature T_{eff} that mediates between dissipation and entropy differs from the local fluid temperature at the particle surface. Because of the long-ranged hydrodynamic correlations, it has to be calculated as the average of the temperature field emanating from the particle weighted by the local dissipation, in the whole solvent

volume. General analytic expressions for T_{eff} are provided by the theory of nonisothermal Brownian motion [31,43].

The effective temperature also quantifies the trade-off between the dissipation due to propulsion, $Q \equiv \langle s \rangle T_{\text{eff}} = \langle j_{\parallel} \rangle v_p \zeta t$, and the squared relative uncertainty in the particle current, $\varepsilon^2 \equiv (\langle j_{\parallel}^2 \rangle - \langle j_{\parallel} \rangle^2) / \langle j_{\parallel} \rangle^2 \simeq 2D / (v_p \langle j_{\parallel} \rangle t)$, namely,

$$\varepsilon^2 Q \simeq 2T_{\text{eff}}. \quad (13)$$

This (saturated) thermodynamic uncertainty relation [44] follows from Eq. (1) and the fact that $P(J_{\parallel})$ is found to be well approximated by a Gaussian.

We finally turn to the validation of the spatial fluctuation theorem, Eq. (2). In a corotating frame, Eq. (5) reads $\dot{\mathbf{r}}' = v_p \mathbf{n}' + \sqrt{2D} \xi_t$ with $\mathbf{r}' = \mathbf{R} \cdot \mathbf{r}$ and $\mathbf{R}(t)$ a time-dependent rotation matrix defined such that $\mathbf{n}' \equiv \mathbf{R} \cdot \mathbf{n}$ is a constant versor arbitrarily chosen as the initial particle orientation. Self-propulsion now shows up as the constant vector $v_p \mathbf{n}'$. Without it, the particle would simply perform isotropic diffusion, and the breaking of this spatial symmetry gives rise to the spatial fluctuation relation (2), as much as the breakdown of time reversibility gives rise to the standard fluctuation theorem (1).

To show this, we follow the procedure leading to Eq. (11), and consider the weights

$$P[\mathcal{M}\mathcal{X}'] \propto \exp\left(-\frac{1}{4D} \int_0^t d\tau [\dot{\mathbf{r}}'(\tau) - v_p \mathbf{M} \cdot \mathbf{n}']^2\right),$$

for paths $\mathcal{M}\mathcal{X}'$ that only differ in the particle orientation $\mathbf{M} \cdot \mathbf{n}'$, where \mathbf{M} is a constant rotation matrix conserving the norm $(\mathbf{M} \cdot \mathbf{n}')^2 = \mathbf{n}'^2 = 1$. They are related by

$$P[\mathcal{X}'] = P[\mathcal{M}\mathcal{X}'] \exp\left(\frac{v_p t}{2D} \mathbf{n}' \cdot (\mathbf{1} - \mathbf{M}^{-1}) \cdot \mathbf{j}[\mathcal{X}']\right), \quad (14)$$

where $P[\mathcal{X}'] = P[\mathcal{M}\mathcal{X}']|_{\mathbf{M}=\mathbf{1}}$, and

$$\mathbf{j}[\mathcal{X}'] \equiv \frac{1}{t} \int_0^t d\tau \dot{\mathbf{r}}'(\tau), \quad (15)$$

is the particle current relative to its instantaneous orientation $\mathbf{n}(t)$. After multiplying Eq. (14) by $\delta(\mathbf{j}[\mathcal{X}'] - \mathbf{J}_1)$ and summing over trajectories, some algebra yields

$$\frac{1}{t} \ln \frac{P(\mathbf{J}_1)}{P(\mathbf{J}_2)} = \frac{v_p}{2D} J(\cos \vartheta_1 - \cos \vartheta_2). \quad (16)$$

This spatial fluctuation relation expresses an exact symmetry between the probabilities to observe currents \mathbf{J}_i of equal magnitude J in different directions specified by their angles ϑ_i with the versor \mathbf{n}' . Its equivalence with Eq. (2) follows from $\mathbf{J}_i \cdot \mathbf{n}' = J \cos \vartheta_i$ by identifying $\mathbf{f} \equiv v_p \mathbf{n}' \zeta / (2T_{\text{eff}})$, where one again recognizes the dissipative nonisothermal driving. Again, it is valid for all times t , provided that the trajectory is sampled on the diffusive time scale. And it contains the scalar fluctuation relation, Eq. (11), as the special case $\vartheta_1 = 0$,

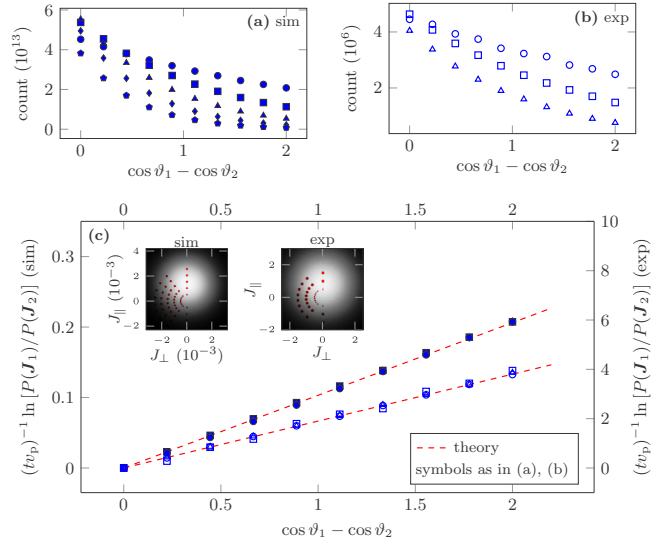


FIG. 3. Upper panel: bin counts for particle current, Eq. (15), for various $J = |\mathbf{J}|$, from simulation (a) and experiment (b). Lower panel: test of the vectorial fluctuation theorem, Eq. (16), using these bin counts as proxies for $P(\mathbf{J})$. Insets: heatmaps for \mathbf{J} , red dots representing the bins from (a) and (b).

$\vartheta_2 = \pi$, i.e., $\mathbf{J}_1 = -\mathbf{J}_2 = J_{\parallel} \mathbf{n}$. Figure 3(c) shows that it is in excellent agreement with our molecular dynamics simulations and experiments.

In summary, we have verified the validity of scalar and vectorial fluctuation relations for a self-propelled colloidal particle suspended in a nonequilibrium solvent. This extends related recent work [29], which could not conclusively settle the issue for the case of an externally driven granular particle. Using a minimal Markovian model, we could recast our results in an intuitive form, revealing that the breaking of the underlying microscopic space-time symmetry is precisely quantified by the entropy production due to swimming. The latter may be written as the energy dissipated to a fictitious equilibrium bath at an effective temperature predicted by the theory of hot Brownian motion. Among all phoretic mechanisms, thermophoresis offers arguably the most critical benchmark because the thermodynamic field that causes the driving (i.e., temperature) is also responsible for nonequilibrium fluctuations. We therefore expect that other types of self-phoretic particles obey the FRs as well. The robustness of the established fluctuation relations against some stochasticity in the driving and the long-term memory and nonequilibrium character of the solvent fluctuations suggests that the assumptions evoked by standard derivations of fluctuation theorems are sufficient, but may actually not all be critical for their successful application.

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Author contributions

Building on previous calculations by M. V. Gnann and D. Ring, in [48] I derived the generalized Langevin equation for hot Brownian motion and studied the violation of the equipartition theorem, taking advice from K. Kroy. In [46] I worked out the underlying theory of fluctuating hydrodynamics in detail so that the order of magnitude of possible corrections to the analytical results could be estimated with confidence. In addition, there I extended the theory to arbitrary temperature gradients, which later (see [57]) allowed us to consider the nonequilibrium fluctuations of a self-thermophoretic colloid. Inspired by discussions with M. Poletti, and C. Pérez-Espigares (from whom I learnt that there was at the time no experimental validation of the spatial fluctuations theorem for 3-dimensional systems), I suggested and supervised the analysis of numerical and experimental data concerning a heated self-propelled particle. I interpreted the results by means of an existing theoretical model which permitted to rationalize the observed validity of the fluctuation relations for the entropy production and particle current. These joint efforts with the experimental group of F. Cichos culminated in [57].

At the same time I started a fruitful collaboration with M. Baiesi. He brought to my attention the unsolved problems encountered in developing the linear response theory of nonequilibrium stochastic systems subjected to thermal perturbation⁶. In [53] and [49] I developed two independent analytical methods to overcome these difficulties, and helped interpreting the numerical results obtained from our model examples. These results were tested in experiments conducted in the lab of S. Ciliberto and A. Petrosyan, where nonequilibrium thermal capacities have been measured for an RC circuit and two hydrodynamically interacting colloids. In [54] and [55] I contributed to the development of the reweighting procedure, the interpretation of the results and the writing. Thanks to the acquired knowledge and expertise in the field of nonequilibrium linear response, I inspired and advised S. Steffenoni in working out the general theory in [56], helped in designing the model examples and interpreting the results, as well as drafted the core parts of the paper.

Long discussions with M. Baiesi on the fluctuation relations resulted in [58]. There, I extended his original ideas (involving jump processes) to diffusive processes, put forward the connection with deterministic dynamical systems (spurred by helpful discussions with L. Rondoni) and expanded the analogy to include jump processes. My interest in dynamical systems had been previously stimulated by some lectures by A. Vulpiani, which G. Saggiorato and I (expanded slightly and) organized into the review [50].

Finally, the research on nonequilibrium virial equation sparked off when M. Baiesi and F. Baldovin showed me numerical results about broken energy equipartition in harmonic chains coupled to multiple thermal baths. I solved the problem analytically and helped interpreting the results obtained for various boundary conditions. Later,

⁶See M. Baiesi, U. Basu, and C. Maes. Thermal response in driven diffusive systems, *Eur. Phys. J. B*, 87:277, 2014.

while developing a perturbative expansion to study anharmonic chains I recognized the generality of the results, set up a concise proof valid for stationary systems with arbitrary interactions, derived the nonequilibrium equation of state and applied it to a well-established model of active matter. These various results appeared in [50] and [46].

Publications

- G. Falasco, M. V. Gnann, D. Rings, and K. Kroy. Effective temperatures of hot brownian motion. *Phys. Rev. E*, 90:032131 (2014).
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