Statistical Thermodynamics for metaequilibrium or metastable states

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Abstract

We show how statistical thermodynamics can be formulated in situations of metaequilibrium or metastability (as in the cases of supercooled liquids or of glasses respectively). By analogy with phenomenological thermodynamics, the primary quantities considered are the heat Q absorbed and the work W performed by the system of interest. These are defined through the energy exchanges which occur when the system is put in contact with a thermostat and with a barostat, the whole system being dealt with as a global Hamiltonian dynamical system. The coefficients of the fundamental form $\delta Q - \delta W$ turn out to have such expressions that the closure of the form is manifest: this gives the first principle. A further step is performed by making use of time reversibility. This provides new expressions for the coefficients, such that the second principle in the form of Clausius is also manifest. Such coefficients are expressed in terms of time–autocorrelations of suitable dynamical variables, in a way analogous to that of Fluctuation Dissipation Theory for equilibrium states. All these results are independent of the ergodicity properties of the global dynamical system.

1   Introduction

In this paper we illustrate an attempt to derive the first two laws of thermodynamics within a statistical mechanics frame, following an approach different from the familiar equilibrium one based on the Gibbs ensembles, which is found in virtually all textbooks (see, for instance, [1]). This for two main reasons.

The first reason is that in many relevant cases the dynamics lacks of strong ergodicity properties, and this casts some doubts on the validity of the usual approach. For example, in the growing field of studies on glassy states, the dynamics is not even supposed to be ergodic, as the so–called "broken ergodicity" occurs. This leads one to look for an approach that should give in any case the thermodynamic principles, while the ergodicity properties of any concrete system should show up only in the time evolution of the relevant thermodynamic quantities.

The second reason is that in the study of metaequilibrium states (as in the case of supercooled liquids) one meets with more than one invariant probability measure. This is due to the existence of several phases, and is usually taken into

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account by introducing a different invariant measure for each phase, in particular the Gibbs measure (expressed in terms of the "true" Hamiltonian) for the stable phase. Now, the laws of phenomenological thermodynamics no doubt apply also for metaequilibrium states, but their deduction from statistical mechanics is currently available only for the Gibbs ensemble. From the practical point of view, one can circumvent this problem by describing the metaequilibrium states too in terms of Gibbs measures, with reference to suitable phenomenological Hamiltonians, one for each different phase. We feel however that a theoretical approach not necessarily based on the use of Gibbs measures may shed some light on this issue.

The fundamental idea underlying the present approach is to formulate statistical thermodynamics in a way that mimics the procedure followed in phenomenological thermodynamics. So the primary quantities to be taken into consideration are the heat Q absorbed and the work W performed by the system of interest, which are measured by putting the system in contact with external devices, such as a thermostat and a barostat. So we have to deal with the corresponding dynamical processes, which we assume to occur, at a phenomenological level, in the following way. One starts from a state in which a temperature T and a pressure p, read on the devices, are attributed to the system of interest too. This is done when a situation of "effective equilibrium" obtains, in which apparently no change occurs anymore in the global system. Then, by purting the system in contact with a thermostat at temperature $T + dT$ and with a barostat at pressure $p + dp$, a change of the state is imposed. One finally waits until a situation of effective equilibrium of the global system is still attained. The coefficients of the fundamental form $\delta Q - \delta W$ are thus measured. Then by the first principle the fundamental form is assumed to be closed, so that the internal energy $U(T, p)$ is defined as a state function by $dU = \delta Q - \delta W$.[1]

So the present approach is characterized by the fact that it makes reference to the "processes" that occur when the system of interest is put in dynamical contact with external devices. In such a way Q and W are directly defined through the energy exchanges of the system with each of the devices. This might appear to be quite abstract. It will be seen, however, that these processes can be mathematically implemented, quite naturally, in such an effective way that the two principles of thermodynamics in their general form easily follow. For what concerns instead the peculiar features of any particular global system (system of interest plus devices), they just show up in the peculiar time dependence of the time correlations of suitable dynamical variables, analogously to what occurs in Fluctuation Dissipation Theory for equilibrium states.

In order to explain the key points of the present approach in the simplest way, in section 2 we consider the paradigmatic case of the process underlying a measurement of the constant–volume heat capacity C_V, which requires the definition of the absorbed heat Q. The general case of a system characterized by two thermodynamic variables, say T and p, is dealt with in section 3, with the corresponding definitions of Q and W. Having thus available an expression for the analogue of the fundamental form $\delta Q - \delta W$ of thermodynamics, we can then tackle the problem of deducing both the first and the second principles. This we do in Section 4 and Section 5 respectively. Then in Section 6 it is shown that

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[1]In equilibrium statistical mechanics, instead, U is a state function just by assumption, being defined as the canonical mean of the Hamiltonian of the system of interest, and δQ is then defined consequently, as $\delta Q = dU + \delta W$, with a previous natural definition of δW.

temperature is an integrating factor for the exchanged heat. Further discussions are given in the conclusive section.

2 The method of processes in the simple paradigmatic case of measurement of the constant–volume heat capacity C_V

A way in which thermodynamics can be thought of is the following (sometimes called by us "Gibbsian approach", see [2]): one is given a thermodynamic potential, for example the free energy $F(T,V)$, which is defined in a domain of the plane T,V, from which all the other thermodynamic functions are obtained, as for instance $C_V = -T\partial_T^2 F$, the heat capacity, or $p = -\partial_V F$, the pressure.

Actually, in phenomenological thermodynamics a different approach is taken (say that of Clausius, Kelvin and Carathéodory). The heat capacity C_V and more in general the coefficients of the differential forms δQ and δW are determined experimentally through suitable measurements, and then, by integration, in virtue of the first and second principle of thermodynamics, the state functions are recovered, in particular the free energy F. On the other hand, the measurements of the coefficients of the fundamental form are performed through suitable "processes". For instance, in the case of C_V the system of interest, previously prepared at a given temperature T, is put in contact with a heat source at temperature $T + dT$: a process is then originated in which heat is exchanged, and C_V is thus measured.

The aim of the present section is to show how a process can be mimicked in statistical mechanical terms, considering the simple paradigmatic case of the measurement of the constant volume heat capacity C_V, which requires to give the definition of the heat Q absorbed by the system of interest. In the next section the case of two thermodynamic parameters will be considered, and the external work W too will be suitably defined.

We consider the system of interest (say, a fluid, enclosed in a fixed cylindrical vessel, of volume V), which is allowed to exchange energy with another system without performing any macroscopic mechanical work. Thus the auxiliary system acts as a thermostat, i.e, a source of heat, which can be exchanged for example through one of the (fixed) bases of the cylinder. For instance, think of an extremely thin separation wall, and let the two systems (say, two fluids) be composed of particles with mutual two–body short–range interactions. In such a case energy exchanges will occur between pairs of particles of the two systems that happen to be sufficiently near to the wall, and such exchanges are not expected to produce macroscopic work.[2]

The global system (system of interest plus thermostat) will be dealt with in a classical Hamiltonian setting, with a given time–independent Hamiltonian. One has a global phase space with canonical coordinates

$$z = (x, x')$$

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[2]Obviously one may think of more realistic models in which each of the two systems separately exchanges heat with the wall. But the example given here may suffice to show that exhanges of energy with no work performed, can be modelel in microscopic terms.

where x are the canonical coordinates of the system of interest, and x' those of the heat source. The total Hamiltonian decomposes as

$$H_{\text{tot}}(z) = H(x) + H_{\text{ther}}(x') + H_{\text{inter}}(z) ,$$

namely, as the sum of the Hamiltonian H of the system of interest, the Hamiltonian H_{ther} of the heat source, and an interaction Hamiltonian H_{inter}. In the model mentioned above (fluids composed of point particles), the Hamiltonians of the two systems contain both the kinetic energy and the potential energy of their particles (two–body short–range potentials), while the interaction Hamiltonian is the sum of two–body short–range potentials between pairs of particles, one belonging to the system and the other one to the thermostat. The flow in the global phase space, induced by the global Hamiltonian H_{tot}, will be denoted by Φ^t.

Due to the interaction term, the energy H of the system of interest will change with time, the changes depending on the initial datum z, and so will do H_{ther}, too. In analogy with the experimental procedure, the exchanged heat Q should be defined as minus the increment of H_{ther} provided by the dynamics. However this in principle depends on the initial datum z. So, as usually done in statistical thermodynamics, we will define Q as the mean of $-\Delta H_{\text{ther}}$ with respect to a suitable probability measure assigned to the initial data, and such a mean value will be expected to represent the typical value of the exchanged energy. This will provide, in our approach, the "mechanical analogue" of Q which takes the place of the familiar one of equilibrium statistical mechanics.

For what concerns the dynamics, along any solution of the equations of motion the total energy is conserved, so that, neglecting the contribution of the interaction Hamiltonian,[3] one has energy conservation in the form

$$[H + H_{\text{ther}}] (\Phi^\tau z) = [H + H_{\text{ther}}] (z) ,$$

or equivalently

$$[\Delta H + \Delta H_{\text{ther}}](z) = 0 , \tag{1}$$

where we have introduced the notation

$$\Delta F(z) \equiv \Delta^\tau F(z) \overset{\text{def}}{=} F(\Phi^\tau z) - F(z) \tag{2}$$

for the change of any dynamical variable F induced by the dynamics at time τ. The observation time τ will be considered as a parameter, and in general will be left understood.

For what concerns the mean value $\langle F \rangle$ of any dynamical variable F, we preliminarily recall, in passing, that there are two equivalent ways of dealing with their time dependence. One is to introduce a time dependence on the measure, induced by the dynamics, i.e., to consider a time dependent probability density evolving according to Liouville equation. The second one, which will be

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[3]As usual it is understood that, for large systems, the interaction Hamiltonian, although playing an essential dynamical role in allowing for energy exchanges between the two subsystems, can nevertheless be neglected in the computations of mean values of the quantities of interest (such as the energy of a subsystem) with respect to a given probability measure. Indeed such quantities are proportional to the volume of the system of interest, whereas the interaction terms are proportional to the area of the basis of the cylinder.

used here, is to fix the measure at its initial value and let the dynamical variable F evolve, according to[4]

$$F_t(z) \stackrel{\text{def}}{=} F(\Phi^t z) \ . \tag{3}$$

We thus come to the choice of the probability measures on the initial data. First we have to describe states of thermodynamic equilibrium or "effective equilibrium", in which the mean values of the macroscopic observables do not evolve with time. For the equilibrium states the usual choice is to describe them with invariant measures. The same choice we make here, leaving understood that invariance should now mean, somehow, practical invariance, and just up to the considered observation time. This actually is a delicate problem. However, the solution proposed here is essentially just the analogue of phenomenological thermodynamics. Choosing a measure which is not invariant, leads instead to a thermodynamic process, in which the mean values may change with time.

The invariant measures for the thermostat at temperature T will be taken to be Gibbs measures with inverse temperature $\beta = 1/k_B T$ (a more general choice will be mentioned later). Instead, a precise choice for the system of interest will not be required for our aims. We only suppose that there exists a one–parameter family $\rho^{syst}(\alpha, x)$ of invariant measures, which is parameterized by an "internal parameter" α that is determined when the mean energy of the system is fixed, in a way analogous to what occurs with the parameter β in the canonical ensemble. The simplest choice is to take for the system of interest a canonical distribution

$$\rho^{syst}(\alpha, x) = \frac{e^{-\alpha H(x)}}{Z(\alpha)} \ . \tag{4}$$

So for the global system we will have a measure with density

$$\rho(T, \alpha; z) = c(T) \, e^{-\beta H_{\text{ther}}(x')} \, \rho^{syst}(\alpha, x) \ ,$$

where the coefficient c obviously is just the inverse of the partition function of the thermostat.

The existence of an equilibrium (or effective equilibrium) state for the global system requires that the internal parameter should have a certain value, say $\overline{\alpha}$, uniquely defined in terms of the "external parameter" (that of the thermostat), namely its temperature T. Thus the reference equilibrium state will have a measure with density

$$\rho(T, \alpha = \overline{\alpha}; z) = c(T) \, e^{-\beta H_{\text{ther}}(x')} \, \rho^{syst}(\overline{\alpha}, x) \tag{5}$$

with $\beta = 1/k_B T$.[5]

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[4]Equivalence of the two procedures is immediately checked. Indeed, writing mean values in terms of a probability density ρ, for the mean value $\langle F \rangle$ of F at time t one has with the first procedure

$$\langle F \rangle = \int F(z) \rho(t, z) \mathrm{d}z \ ,$$

where ρ evolves according to the Liouville theorem, i.e., with $\rho(t, z) = \rho(0, \Phi^{-t} z)$. On the other hand the Jacobian determinant of $z' = \Phi^{-t} z$ has value 1, so that, by changing variables (and calling again z the new variable z') one has the dual form

$$\langle F \rangle = \int F(\Phi^t z) \rho(0, z) \mathrm{d}z \equiv \int F_t(z) \rho(0, z) \mathrm{d}z \ .$$

[5]We are assuming that neglecting the interaction term in the measure introduces only very small errors in computing the mean values of the quantities of interest.

We are however interested in the thermodynamic process, which is started by putting the system in contact with external devices at changed values of the parameter, and we mimic such a situation by choosing as initial measure for the global system the nonequilibrium one with density

$$\rho(T + dT, \overline{\alpha}; z) = c(T + dT)e^{-[\beta + d\beta]H_{\text{ther}}} \rho^{syst}(\overline{\alpha}) \ , \tag{6}$$

in which the value $\overline{\alpha}$ of the internal parameter was left unchanged. Due to the insuing energy exchanges one expects that the dynamics will lead to a possible approach to a new state of equilibrium or effective equilibrium.

Mean values with respect to the noninvariant measure will denoted by $\langle \cdot \rangle^{\text{neq}}$. Mean values with respect to the invariant measure might be denoted by $\langle \cdot \rangle^{\text{eq}}$, but actually will be simply denoted by $\langle \cdot \rangle$:

$$\left\langle F \right\rangle^{\text{neq}} \stackrel{\text{def}}{=} \int F(z)\,\rho(T + dT, \overline{\alpha}; z)\,dz \ , \tag{7}$$

$$\left\langle F \right\rangle \equiv \left\langle F \right\rangle^{\text{eq}} \stackrel{\text{def}}{=} \int F(z)\,\rho(T, \overline{\alpha}; z)\,dz \ , \tag{8}$$

As previously discussed, we define the heat Q absorbed by the system of interest by

$$Q \stackrel{\text{def}}{=} - \left\langle \Delta H_{\text{ther}} \right\rangle^{\text{neq}} \ , \tag{9}$$

namely,

$$Q \stackrel{\text{def}}{=} \left\langle \Delta H \right\rangle^{\text{neq}} \equiv - \int \Delta H_{\text{ther}}(z)\,\rho(T + dT, \overline{\alpha}; z)\,dz \ .$$

This, quite natural, definition of the statistical mechanical analogue of the absorbed heat, is the key ingredient of the present approach.

From this, δQ is immediately obtained by expanding Q to first order in dT. Recalling that the equilibrium mean value of ΔH vanishes, $\langle \Delta H \rangle = 0$. one thus gets

$$\delta Q = C_V dT \tag{10}$$

where the constant–volume heat capacity C_V has the expression

$$C_V = - \int \Delta H_{\text{ther}}(z)\,\partial_T \rho(T, \overline{\alpha}; z)\,dz \ . \tag{11}$$

Notice that the proportionality of δQ to dT exhibits the fact that the thermodynamic state variable of the system of interest is indeed T, and not the internal parameter α, as one might be tempted to suppose. This is at variance with what occurs in equilibrium statistical thermodynamics, in which an external parameter does not even exist. This is however in agreement with phenomenological thermodynamics, in which the values of the state variables are those of the external devices and not those of the system of interest which, during the process, might not even be defined. For a discussion of this point in the frame of thermodynamics of processes, see [1], §20 and §21.

In the next section, when the general case will be considered, the fundamental differential form will be determined in an analogous way, and its coefficients will have expressions analogous to (11). Using this fact, the first principle will be immediately proved.

Then, another key point will be introduced, which amounts to exploiting the time–reversibility of the Hamiltonian flow. This leads to a general lemma which, for any dynamical variable F (even in the momenta of the particles constituting the system) gives

$$\int \Delta F \, \frac{\partial}{\partial \beta} \rho \, \mathrm{d}z = \frac{1}{2} \left\langle \Delta F \, \Delta H_{\text{ther}} \right\rangle \, . \tag{12}$$

With $\partial_T = -(1/k_B T^2)\partial_\beta$, this gives for the heat capacity C_V the new expression

$$C_V = \frac{1}{2} \frac{1}{k_B T^2} \left\langle \left(\Delta H_{\text{ther}} \right)^2 \right\rangle \, , \tag{13}$$

or also, due to energy conservation, the ezpression

$$C_V = \frac{1}{2} \frac{1}{k_B T^2} \left\langle \left(\Delta H \right)^2 \right\rangle \, , \tag{14}$$

written in terms of the energy of the system of interest. A deduction of this formula in the frame of FD theory for equilibrium states, described by Gibbs measures, was given in [3].

Formula (14), which exploits the time–reversal invariance of the system, has two deep consequences. The first one is that it makes immediately apparent that one has the property

$$C_V \geq 0 \, ,$$

which in turn, as is immediately evident, constitutes a proof of the second principle of thermodynamics in the form of Clausius.

The second consequence becomes apparent after a very simple rearrangement of the formula. Expand the square $(\Delta H)^2 = (H_\tau - H)^2$, and add and subtract the term $\langle H^2 \rangle$. Then the formula immediately becomes

$$C_V = \frac{1}{k_B T^2} \left[\sigma_H^2 - \mathscr{C}_H(\tau) \right] \, , \tag{15}$$

where σ_F^2 denotes the variance of F with respect to the reference invariant measure, and

$$\mathscr{C}_F(\tau) \overset{\text{def}}{=} \left\langle F(\Phi^\tau z) F(z) \right\rangle - \left\langle F \right\rangle^2 \tag{16}$$

is the corresponding time–autocorrelation function.

So, on the one hand one sees that the dependence of the heat capacity on the observation time occurs through the time–correlation function of the energy H of the system of interest. On the other hand, formula (13) generalizes the familiar Boltzmann–Einstein equilibrium expression for the heat capacity in the canonical ensemble

$$C_V^{eq} = \frac{1}{k_B T^2} \sigma_H^2 \, . \tag{17}$$

Indeed it shows that the value of the heat capacity measured at the observation time τ reduces to a form similar to the canonical one when (and if) the time–autocorrelation of the energy H of the system of interest vanishes.

This is the place where the ergodicity properties show up. Indeed it might occur that, within a macroscopically relevant observation time, the autocorrelation relaxes to zero. But it might also occur that it relaxes to a well definite non vanishing value. Or even that no relaxation to any definite value is observed.

Phenomena of this kind were experimentally observed for ice (see [4]), for the propagation of ultrasonic waves (see [5]) and for glasses (cf. [6]). Theoretical works proving no–decay properties of time–correlation functions (even in the thermodynamic limit) up to relevant times are available since some time (see [7, 8]), while corresponding computational works are available since a longer time (see [9, 10]).

The idea that dynamics may be relevant for the mathematical description of the process underlying a macroscopic measurement should be considered as corresponding to an actual physical property, and has in fact a long history. This is quite vividly witnessed by a quotation from W. Nernst. When in the year 1911 he started a series of systematic measurements of the heat capacities of solids at low temperatures, he found out that, as temperature was decreased, the time required for a stabilization of the measurement increased so much that at a certain moment he even started doubting that an actual value for the measurement may exist. However, quite unexpectedly, he finally found out that, by further decreasing the temperature, the time required for getting some definite value became shorter. See [11] and [12].

3   The general case

The key feature which allowed us to obtain formula (11) for the heat capacity C_V in the previous section was that the flow Φ^t does not depend on temperature T, so that the choice of temperature influences only the probability measure. So, in order to compute the derivative $\partial_T \langle F \rangle$ of a dynamical variable, as we did in dealing with the heat capacity C_V, one only has to take the derivative of the density of the initial measure. Things seem to be different if, instead of temperature, one changes an external parameter such as volume V, because in such a case the Hamiltonian depends on the external parameter, so that the flow Φ^t is no more independent of the considered process, i.e., of the time variation of the external parameter. For example, by changing the volume of the system by an amount dV, the Hamiltonian H is changed to $H + (\partial_V H)\, dV$, so that the time evolution depends on the variation of the external parameter. This is the approach usually followed in FD theory, and in such a way strong ergodicity properties are required of the dynamics in order to prove the validity of thermodynamic laws (see [13]). In order to avoid the need of ergodicity properties in deriving themodynamics, we chose to include the devices (which cause the changes of the mechanical parameter) as parts of the global Hamiltonian system to be studied, in analogy with what we did in the previous section with the heat source. In such a way, it will be seen that the partial derivatives of the mean values with respect to the parameters, still reduce to derivatives of the initial density. This will allow for the derivation of the first two principles without invoking ergodicity properties.

So, we consider the system of interest (say, a fluid) enclosed in a cylindrical vessel in contact with a heat source through one of the bases which remains fixed, while the other basis is a movable piston (see [14], or [15], page 131), in contact with a work source. We model the piston as a rigid body of macroscopic mass M and position l (measured from the fixed wall), so that to any position l there corresponds a volume $V = Al$ of the system of interest, A being the area of the piston. In such a way, V does not appear as an external parameter, but

as a dynamical variable (a function of coordinates and momenta) of the global considered system. So, through the two bases of the cylinder the system of interest (or "internal system") can exchange energy with the two other systems (or "external ones"), a thermostat which acts, as in the previous section, as a source of heat (through the fixed basis), and a barostat which acts as a source of purely mechanical, or adiabatic, work (through the movable piston). It is well known [16] that in dynamical terms the adiabaticity condition is satisfied up to extremely long times if the piston is modeled as a single rigid particle of macroscopic mass, and the particles of the barostat do not interact directly with those of the system of interest. The latter condition is satisfied by assuming a short range pair potential between particles and letting the piston be thick enough. The two auxiliary systems are thought of as having no direct mutual interaction.

The global system (system of interest plus sources of heat and of work) is dealt with in a classical Hamiltonian setting, with a given time independent Hamiltonian and a fixed global geometry, the position of the piston being considered as one of the configurational coordinates of the global system. One thus has a global phase space with canonical coordinates

$$z = (x, x', x'', l, p_l)$$

where x are the canonical coordinates of the system of interest, x' those of the heat source, x'' those of the work source, l the distance of the piston from the fixed wall, and p_l the corresponding conjugate momentum. The total Hamiltonian decomposes as

$$H_{\text{tot}}(z) = H(x, l) + H_{\text{ther}}(x') + H_{\text{bar}}(x'', l) + H_{\text{inter}}(z) .$$

Here H is the partial Hamiltonian of the system of interest, while H_{ther}, and H_{bar} are the partial Hamiltonians of the sources, the labels *ther* and *bar* standing for thermostat and barostat respectively. Finally there appears an interaction Hamiltonian, which contains, besides the interaction between the system and the heat source, also a term of the form $p_l^2/2M$ for the kinetic energy of the piston, dealt with as a single rigid particle of mass M of macroscopic size. The flow in the global phase space is thus well defined, and will still be denoted by Φ^t. In particular, the volume V will evolve as any other dynamical variable once the initial datum z has been fixed.

For what concerns probability measures of the global system, we will still start considering invariant or effectively invariant reference measures. Processes will then be obtained by considering perturbations of them. So we have to consider a family of measures relative to the global system. The family depends on two "external" thermodynamic parameters relative to the sources, i.e., temperature T for the heat source, and pressure p for the work source. Typically one can take for the thermostat a Gibbs distribution with inverse temperature β, and for the barostat a Gibbs measure with a suitable inverse temperature β_{bar} (independent of β), which determines p.

Furthermore, one needs two "internal" parameters, say $\alpha = (\alpha_1, \alpha_2)$, relative to the system of interest, related, respectively, to its mean energy and to the mean value of the coordinate l of the piston.[6] The simplest example is to take

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[6]A larger number of internal parameters may be required in more general cases, as for example in the case of a nonhomogeneous fluid.

a probability density analogous to the canonical one (4) of the previous section, namely, the canonical–barostatic ensemble with parameters $(\tilde{\beta}, \tilde{p})$,

$$\frac{\exp(-\tilde{\beta}(H + \tilde{p}Al))}{Z(\tilde{\beta}, \tilde{p})} \ , \tag{18}$$

where Z denotes the normalization constant and the Lagrange multiplier $\tilde{p}$ fixes the mean value of l. So the family for the global system will have densities of the form

$$\rho(T, p, \alpha; z) \ .$$

Concerning the reference state, we now assume that, for any pair (T, p) of external thermodynamic parameters, there exists an equilibrium (or effective equilibrium) state of the global system, which corresponds to some definite values $\overline{\alpha} = \overline{\alpha}(T, p)$ of the internal parameters α for which the measure is invariant or effectively invariant. Notice that, as already pointed out in section 2, the thermodynamic state variables (T, p) of the system of interest are just those of the external devices.

Given one such reference state with density

$$\rho(T, p, \overline{\alpha}; z) \ , \tag{19}$$

we then introduce the state in which the external parameters have been suddenly changed from (T, p) to $(T+\mathrm{d}T, p+\mathrm{d}p)$, *while the values of the internal parameters are kept constant.* The corresponding initial measure will then have a density

$$\rho(T + \mathrm{d}T, p + \mathrm{d}p, \overline{\alpha}; z) \ . \tag{20}$$

In general such a measure will not be invariant, i.e., will correspond to a nonequilibrium situation, determining a process which could possibly lead, at the very end, to a new equilibrium state, with a different value $\overline{\alpha} + \mathrm{d}\alpha$ of the internal parameter.

We now have to estimate the energy exchanges between the system of interest and each of the sources, namely, the heat Q absorbed by the system, and the work W performed by it.

From dynamics, energy conservation now follows in the form

$$[H + H_{\mathrm{ther}} + H_{\mathrm{bar}}](\Phi^\tau z) = [H + H_{\mathrm{ther}} + H_{\mathrm{bar}}](z) \ ,$$

or equivalently, with ΔF defined by (2),

$$[\Delta H + \Delta H_{\mathrm{ther}} + \Delta H_{\mathrm{bar}}](z) = 0 \ , \tag{21}$$

the interaction energy still having been neglected.[7]

As in the previous section, the heat Q absorbed by the system of interest is defined by

$$Q \stackrel{\mathrm{def}}{=} -\left\langle \Delta H_{\mathrm{ther}} \right\rangle^{\mathrm{neq}} \ , \tag{22}$$

which explicitly becomes

$$Q = -\int \Delta H_{\mathrm{ther}}(z) \, \rho(T + \mathrm{d}T, p + \mathrm{d}p, \, \overline{\alpha}; z) \, \mathrm{d}z \ .$$

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[7] In order to neglect the interaction Hamiltonian in computing averages one requires to assume not only (as usual) that the system is large, but also that motions are considered in which the piston moves very slowly.

Analogously we introduce for the work W performed by the system the definition

$$W \stackrel{\text{def}}{=} \langle \Delta H_{bar} \rangle^{\text{neq}} . \tag{23}$$

As in the previous section, mean values with respect to the noninvariant measure with density (20) are denoted by $\langle \cdot \rangle^{\text{neq}}$, while those referring to the invariant measure with density (19) are simply denoted by $\langle \cdot \rangle$.

4 Deduction of the first principle

We can now come to the first principle. From the definitions (22) and (23) of Q and W, and from energy conservation (21), one gets

$$\begin{aligned} Q - W &= \langle \Delta H \rangle^{\text{neq}} \\ &\equiv \int \Delta H(z)\, \rho(T + \mathrm{d}T, p + \mathrm{d}p, \overline{\alpha}; z)\, \mathrm{d}z . \end{aligned} \tag{24}$$

Then, by expanding ρ to first order in $\mathrm{d}T$ and $\mathrm{d}p$, differential forms δQ and δW remain thus defined. So the analogue of the fundamental form $\delta Q - \delta W$ turns out to be expressed in terms of the changes ΔH of the Hamiltonian of the system of interest only (although still in terms of a measure involving the two sources), being given by

$$\delta Q - \delta W = c_1(T, p)\, \mathrm{d}T + c_2(T, p)\, \mathrm{d}p , \tag{25}$$

with coefficients

$$\begin{aligned} c_1 &\stackrel{\text{def}}{=} \int \Delta H(z)\, \frac{\partial}{\partial T} \rho(T, p, \overline{\alpha}; z) \mathrm{d}z , \\ c_2 &\stackrel{\text{def}}{=} \int \Delta H(z)\, \frac{\partial}{\partial p} \rho(T, p, \overline{\alpha}; z) \mathrm{d}z . \end{aligned} \tag{26}$$

Proving the first principle amounts to proving that the differential form $\delta Q - \delta W$ is closed. On the other hand, the variables T and p enter the integrals at the right hand side of (26) only through the factor $\frac{\partial}{\partial T} \rho$ or the factor $\frac{\partial}{\partial p} \rho$. Thus, assuming that the density ρ is smooth enough in the parameters, one has

$$\frac{\partial c_1}{\partial p} = \frac{\partial c_2}{\partial T} ,$$

which is the analogue of a Maxwell relation. So the form $\delta Q - \delta W$ is closed, and there exists (at least locally) a function $U = U(T, p)$ such that $\delta Q - \delta W = \mathrm{d}U$. So the internal energy can be defined by integrating the differential form (25). The first principle is thus proven. Notice that the proof is obtained here without any assumption of ergodic type on the dynamics, just because in our approach changes in the external parameters involve changes in the measures only.

We close this section with two remarks. The first one concerns the fact that the internal energy U cannot be expressed as the mean of the energy H with respect to the reference invariant measure. For example, the state function $\tilde{U}$ defined by

$$\tilde{U} = \int H(z)\, \rho(T, p, \overline{\alpha}; z) \mathrm{d}z$$

produces a differential form

$$\mathrm{d}\tilde{U} = \tilde{c}_1(T,p)\,\mathrm{d}T + \tilde{c}_2(T,p)\,\mathrm{d}p \; , \tag{27}$$

with coefficients

$$
\begin{aligned}
\tilde{c}_1 &\stackrel{\mathrm{def}}{=} \int H(z)\,\frac{\partial}{\partial T}\rho(T,p,\overline{\alpha};z)\mathrm{d}z \; , \\
\tilde{c}_2 &\stackrel{\mathrm{def}}{=} \int H(z)\,\frac{\partial}{\partial p}\rho(T,p,\overline{\alpha};z)\mathrm{d}z
\end{aligned}
\tag{28}
$$

which, at variance with (26), involve integrals of H rather than of ΔH.

The second remark concerns the relation between the dynamical increment of internal energy

$$\Delta^\tau U \stackrel{\mathrm{def}}{=} Q - W \tag{29}$$

defined through (24) – in correspondence to increments $\mathrm{d}T$, $\mathrm{d}p$ of the parameters – and the increment of the equilibrium internal energy which is obtained by incrementing the parameters T and p in the reference equilibrium measure. This relation is obtained by remarking that the definition (24), which involves the time evolved $H_\tau(z) \equiv H(\Phi^\tau z)$ of the dynamical variable H while keeping fixed the measure, can also be dually expressed by letting the measure evolve with time, while keeping fixed the dynamical variable H:

$$
\begin{aligned}
\Delta^\tau U = \int H(z)\Big[&\rho(T+\mathrm{d}T,p+\mathrm{d}p,\overline{\alpha};\Phi^{-\tau}z) \\
&- \rho(T+\mathrm{d}T,p+\mathrm{d}p,\overline{\alpha};z)\Big]\mathrm{d}z \; .
\end{aligned}
\tag{30}
$$

Thus, if the density ρ tends (in weak sense) to a final equilibrium density, with the internal parameters α adapted to the new external ones, and if in addition it factors into an external part and an internal one (as was assumed of the initial density, too), then one should have $\Delta^\tau U \to \langle H\rangle_{T',p'} - \langle H\rangle_{T,p}$ with $T' = T+\mathrm{d}T$, $p' = p+\mathrm{d}p$, i.e.,

$$\langle H\rangle_{T,p} + \Delta^\tau U \to \langle H\rangle_{T',p'} \; ,$$

where $\langle\,\cdot\,\rangle_{T,p}$ denotes mean value over the phase space of the system of interest, with respect to the canonical–barostatic ensemble at values T, p of the external parameters.

So the time–dependent family $\Delta^\tau U$ considered here provides an interpolation $\langle H\rangle_{T,p} + \Delta^\tau U$ between the initial effective–equilibrium value $\langle H\rangle_{T,p}$ and the final effective–equilibrium one $\langle H\rangle_{T',p'}$ of the internal energy. However, it is left to the dynamics to decide whether, and at which time, will the final equilibrium value be actually attained.

5 The second principle as a consequence of microscopic time–reversibility.

The result proved in the previous section, according to which in general the internal energy of metaequilibrium thermodynamics cannot be expressed as the

mean of the Hamiltonian with respect to the reference invariant measure, is the one to which we attach a particular significance.

We leave aside, however, general problems of such a type, and continue the discussion of metaequilibrium thermodynamics. We thus come to discussing how the second principle too is obtained. To this end we will show that the coefficients of the form δQ can be expressed in terms of suitable correlation functions, as usually occurs in FD theory. This fact is obtained if the further assumptions are made that i) the dynamics is time reversible, and that ii) the sources are described by Gibbs measures. The latter condition can actually be weakened, as will be mentioned later.

So, let us recall the time–reversibility property. This property amounts to requiring that there exists a mapping $\mathcal{P}$ of phase space onto itself (inverting the sign of the velocities of all particles that constitute the global system) with the properties

$$\mathcal{P}^2 = \mathcal{I} \ , \quad (\mathcal{P}\Phi^\tau)^2 = \mathcal{I} \ ,$$

where $\mathcal{I}$ is the identity map. It is well known that the reversibility property is satisfied by essentially all systems of interest, namely, those with Hamiltonians even in the momenta of the particles. So in particular in our case we will have

$$H_{\text{tot}}(\mathcal{P}z) = H_{tot}(z) \ , \quad H(\mathcal{P}z) = H(z) \ ,$$
$$H_{\text{ther}}(\mathcal{P}z) = H_{\text{ther}}(z) \ , \quad H_{bar}(\mathcal{P}z) = H_{bar}(z) \quad .$$

Concerning the family of measures for the initial data, we will assume that the reference invariant measures have the form

$$\rho(\beta, \beta_{\text{bar}}, \overline{\alpha}, z)$$
$$= c(\beta, \beta_{\text{bar}}) \ e^{-\beta H_{\text{ther}}} \ e^{-\beta_{\text{bar}} H_{\text{bar}}} \ \rho^{\text{syst}}(\overline{\alpha}; z) \ , \tag{31}$$

where ρ^{syst} refers to the system of interest, $c(\beta, \beta_{\text{bar}})$ is the familiar normalization factor involving the partition functions of the sources, while β and β_{bar} are Lagrange multipliers which determine the temperature T of the thermostat and the temperature of the barostat (and so implicitly its pressure too). Obviously the invariance with respect to $\mathcal{P}$ will be required to hold also with respect to the considered measure.

On account of reversibility, one has the following

Lemma: *Let the global Hamiltonian system be time–reversible, and let the reference invariant measure have a density of the form (31). Then, for any dynamical variable F having the property*

$$F(\mathcal{P}z) = F(z) \ , \tag{32}$$

one has

$$\int \Delta F \ \frac{\partial}{\partial \beta} \rho \, \mathrm{d}z = \frac{1}{2} \left\langle \Delta F \ \Delta H_{\text{ther}} \right\rangle$$
$$\int \Delta F \ \frac{\partial}{\partial \beta_{\text{bar}}} \rho \, \mathrm{d}z = \frac{1}{2} \left\langle \Delta F \ \Delta H_{\text{bar}} \right\rangle \ . \tag{33}$$

The proof, for example for the first formula, is as follows. Due to the exponential form of ρ with respect to the sources one has

$$\int \Delta F \ \frac{\partial}{\partial \beta} \rho \, \mathrm{d}z = - \int \Delta F(z) H_{\text{ther}}(z) \rho(z) \mathrm{d}z \ .$$

13

Notice that, in performing the partial differentiation, one further term would appear, which contains the derivative of the normalization factor $c(\beta, \beta_{\text{bar}})$. However, being proportional to $\langle \Delta F \rangle$, such a further term vanishes, in virtue of the invariance of the considered measure.[8] Introduce then the change of variables

$$z = \mathcal{P}\Phi^\tau y$$

which is canonical, so that $\mathrm{d}z = \mathrm{d}y$. Use (32), which implies

$$\Delta F(z) = -\Delta F(y) \ ,$$

and use also the invariance of the reference measure, $\rho(z) = \rho(y)$. Thus, calling again by z the dummy variable y one gets

$$\int \Delta F \ \frac{\partial}{\partial \beta} \rho \, \mathrm{d}z = \int \Delta F(z) H_{\text{ther}}(\mathcal{P}\Phi^\tau z)\rho(z)\mathrm{d}z \ .$$

Finally, the result follows by taking the semisum of the original expression and of the last one. The second formula is proved analogously.

We can now come to the second principle. By expanding the nonequilibrium density to first order in $\mathrm{d}\beta$ and $\mathrm{d}\beta_{\text{bar}}$ in formula (22) for the exchanged heat, one gets for the differential form δQ the expression

$$\delta Q = q_1(\beta, \beta_{\text{bar}}) \, \mathrm{d}\beta + q_2(\beta, \beta_{\text{bar}}) \, \mathrm{d}\beta_{\text{bar}} \ , \tag{34}$$

with coefficients given by

$$
\begin{aligned}
q_1 &\overset{\text{def}}{=} -\int \Delta H_{\text{ther}}(z) \ \frac{\partial}{\partial \beta} \rho(\beta, \beta_{\text{bar}}, \overline{\alpha}; z)\mathrm{d}z \ , \\
q_2 &\overset{\text{def}}{=} -\int \Delta H_{\text{ther}}(z) \ \frac{\partial}{\partial \beta_{\text{bar}}} \rho(\beta, \beta_{\text{bar}}, \overline{\alpha}; z)\mathrm{d}z \ .
\end{aligned}
\tag{35}
$$

Since $\frac{\partial}{\partial T} = -1/(k_B T^2)\frac{\partial}{\partial \beta}$, the Lemma shows immediately that the heat capacity C_p, at constant β_{bar} (i.e., at constant pressure) is positive,

$$C_p = \frac{1}{2k_B T^2} \big\langle \left[\Delta H_{\text{ther}}\right]^2 \big\rangle \geq 0 \ . \tag{36}$$

Thus the second principle in the Clausius form (heat spontaneously flows from hot to cold bodies) is proven. By the way, one is naturally led to guess that the second principle may not hold if microscopic time–reversibility were not satisfied.[9]

Our aim is now to find expressions for δW and for δQ in terms of dynamical variables of the system of interest, analogously to what was done in section 2 when passing from (13) to (14) in connection with C_V. First of all the equilibrium pressure p is defined as usual (see [15]) as the equilibrium mean value

---

[8]This is the reason why relations (33) hold if one considers ΔF and not just F.

[9]The positiveness of the heat capacity was proven above, making use of the assumption that the marginal measure for the environment be of Gibbs type. However, if one looks at the proof one realizes that the result also holds if any assumption is made which guarantees that the partial derivatives of the density ρ have negative definite sign. For example, a sufficient condition is that, in formula (31) for the density, instead of the exponential $\exp(-\beta H)$ there appears a factor $f(\beta H)$, with any function f having the property $f' \leq 0$.

of the corresponding dynamical variable $P(z) \stackrel{\text{def}}{=} -\frac{\partial H}{\partial V}(z) = -\frac{1}{A}\frac{\partial H}{\partial l}(z)$. So the pressure p is given by

$$p = \langle P \rangle = -\langle \frac{\partial H}{\partial V} \rangle = \langle \frac{\partial H_{\text{bar}}}{\partial V} \rangle \ .$$

Thus the work performed by the system of interest on the barostat should be given by

$$\delta W = p\langle \Delta V \rangle^{\text{neq}} \ . \tag{37}$$

This can also be seen by using the definition (23) of work and the approximation, valid for small ΔV,

$$\Delta H_{\text{bar}} = p\Delta V \ .$$

The heat δQ absorbed by the system of interest can be expressed in terms of dynamical variables of the system of interest as

$$\delta Q = \langle \Delta(H + pV) \rangle^{\text{neq}} \ ,$$

since one has

$$\Delta H_{\text{ther}} = -\Delta H - \Delta H_{\text{bar}} = -\Delta(H + pV) \ .$$

Thus, in virtue of the Lemma, the coefficients q_1, q_2 (see (35)) of the form δQ turn out to have the form

$$\begin{aligned} q_1 &= -\frac{1}{2}\langle [\Delta(H + pV)]^2 \rangle \\ q_2 &= \frac{p}{2}\langle \Delta(H + pV)\, \Delta V \rangle \ . \end{aligned} \tag{38}$$

The previous relations show that the thermodynamic quantities q_1, q_2 are expressed in terms of correlation functions with respect to the reference invariant measure. For example, in the case of the heat capacity C_p given by (36), by expanding the square

$$[\Delta(H + pV)(z)]^2 = [(H + pV)(\Phi^\tau z) - (H + pV)(z)]^2$$

and adding and subtracting the term $\langle H + pV \rangle^2$ one immediately gets

$$C_p = \frac{1}{k_B T^2}\left[\sigma_{H+pV}^2 - \mathscr{C}_{H+pV}(\tau)\right] \ , \tag{39}$$

where σ_F^2 denotes the variance of F with respect to the reference effective–equilibrium measure, and $\mathscr{C}_F(\tau) \stackrel{\text{def}}{=} \langle F(\Phi^\tau z)F(z) \rangle - \langle F \rangle^2$ its time–autocorrelation function. This exhibits that C_p attains a time–indpendent value only if the correlation $\mathscr{C}_F(\tau)$ converges to a definite value. Moreover C_p assumes a form which is similar to the canonical one if such a correlation decays to zero.

6 The temperature of the thermostat as an integrating denominator for δQ

Thus, having proven the second principle, we know that an integrating denominator for the differential form δQ exists. One may ask however whether such

an integrating denominator coincides with the temperature of the thermostat. We will show now that this is actually the case, at least if the observation time τ is sufficiently large to guarantee that a suitable dynamical decorrelation did occur.

So, let us consider the form

$$\beta \delta Q = \beta q_1 \, \mathrm{d}\beta + \beta q_2 \, \mathrm{d}\beta_{\mathrm{bar}} \ , \tag{40}$$

where the coefficients q_1 and q_2 are defined by (35), and let us investigate whether it is closed. This requires calculating $\frac{\partial(\beta q_1)}{\partial \beta_{\mathrm{bar}}} - \frac{\partial(\beta q_2)}{\partial \beta}$. As in the case of the internal energy, again one finds that the two terms involving the second derivatives of ρ cancel, so that one remains with

$$\begin{aligned}
&\frac{\partial(\beta q_1)}{\partial \beta_{\mathrm{bar}}} - \frac{\partial(\beta q_2)}{\partial \beta} \\
&= \beta \frac{\partial p}{\partial \beta_{\mathrm{bar}}} \int \Delta V(z) \, \frac{\partial}{\partial \beta} \, \rho \, \mathrm{d}z \\
&\quad - \int \Delta(H + pV)(z) \, \frac{\partial}{\partial \beta_{\mathrm{bar}}} \, \rho \, \mathrm{d}z \ .
\end{aligned} \tag{41}$$

So, using the Lemma one gets

$$\begin{aligned}
&\left[\frac{\partial(\beta q_1)}{\partial \beta_{\mathrm{bar}}} - \frac{\partial(\beta q_2)}{\partial \beta} \right] \\
&= -\frac{1}{2} \big\langle \Delta V \, \Delta(H + pV) \big\rangle \, \left(\beta \frac{\partial p}{\partial \beta_{\mathrm{bar}}} + p \right) \ .
\end{aligned} \tag{42}$$

Thus the form is closed if one has

$$\frac{\partial p}{\partial \beta_{\mathrm{bar}}} = -\frac{p}{\beta} \ . \tag{43}$$

To investigate this point requires finding the expression of $\frac{\partial p}{\partial \beta_{\mathrm{bar}}}$, and this is obtained by finding the expression of $\mathrm{d}p$ as a differential form with respect to $\mathrm{d}\beta$, $\mathrm{d}\beta_{\mathrm{bar}}$. In analogy with what previously done for other differential forms, we just define $\mathrm{d}p$ as the first order expansion of $\langle \Delta P \rangle^{\mathrm{neq}}$ with respect to $\mathrm{d}\beta$, $\mathrm{d}\beta_{\mathrm{bar}}$. This gives, using again the Lemma,

$$\mathrm{d}p = -\frac{1}{2} \big\langle \Delta P \Delta(H + pV) \big\rangle \mathrm{d}\beta + \frac{p}{2} \big\langle \Delta P \Delta V \big\rangle \mathrm{d}\beta_{\mathrm{bar}} \tag{44}$$

from which one gets

$$\frac{\partial p}{\partial \beta_{\mathrm{bar}}} = \frac{p}{2} \big\langle \Delta P \Delta V \big\rangle \ . \tag{45}$$

On the other hand, if a suitable decorrelation occurs, one has as usual

$$\frac{1}{2} \big\langle \Delta P \Delta V \big\rangle \to \big\langle \left(P - \langle P \rangle \right) \left(V - \langle V \rangle \right) \big\rangle \ . \tag{46}$$

Finally, the r.h.s. of (46) is just equal to $-1/\beta$, as one finds in the Landau–Lifshitz textbook [1].

Thus after a sufficiently long time the temperature of the thermostat is an integrating denominator of the form δQ. It is presumable however that such a relaxation time might in general be rather short, especially in comparison with the relaxation times of other quantities.

7 Conclusions

In this paper we have shown how it is possible to formulate statistical thermodynamics in terms of the processes induced by a change of their thermodynamic parameters. This is at variance with the familiar approach in which thermodynamics is deduced once a fundamental thermodynamic function (such as internal energy or free energy) has been defined through a given equilibrium measure. A characteristic feature of our approach is that it allows one to deal also with metaequilibrium or metastability situations in which the relevant time–correlations do not decay to zero. In any case, in order to have a complete theory, a major problem remains, namely, how to formulate and possibly prove the zeroth principle, i.e., the transitivity of the (meta)equilibrium. A short discussion is reported below.

A relevant feature of the present approach is that it involves in a substantial way, in addition to the system of interest, also the measurement devices. Consequently, one has the problem of understanding whether a physical, actually measured, property belongs to the system of interest or rather depends on the measuring procedure too. Standard equilibrium statistical thermodynamics, being formulated in terms of the Hamiltonian of the system of interest only, avoids in principle any reference to the method of measurement, and perhaps one would be tempted to say that this is indeed correct. In general, however, things are not so. And actually, in the work [6], of which it was said that it gave rise to a new epoch of thermodynamics, one even finds the sentence: *"How does one interpret a quantity such as the specific heat in a nonequilibrium situation? Clearly, the dynamics of how one performs the measurement enters into the measured value"*. This circumstance finds a counterpart in the present approach. Indeed the thermodynamic quantities we are considering, typically the heat capacity of the system of interest, are in general represented by expressions which involve not only the system of interest, but also the sources. So the measured quantities in general depend on the measurement procedure, and the dependence disappears only when a suitable relaxation has occurred, if indeed it takes place.

However, the main interest of the proposal made here is perhaps that it may provide an answer to a question of principle that remains open within the equilibrium approach. The problem is to understand how many degrees of freedom should be attributed to a microscopic model. Indeed there can exist degrees of freedom that, though contibuting to the mean canonical energy, do not contribute to the exchanged energy up to the considered measurement time (i.e., are practically "frozen"), and so can be neglected from a thermodynamical point of view. A typical example is the one often mentioned by Boltzmann, namely, the rotational energy of a perfectly smooth sphere , which does not contribute to the specific heat.

It is just in this connection that a difficulty arises with the zeroth principle, as previously mentioned. Indeed, it may happen that two different systems (call them system 1 and system 2) appear to be in equilibrium with a third one, when they are put separately in contact with it, but some degrees of freedom of such two systems remain frozen during the interaction up to the observation time. If, however, the same degrees of freedom do exchange energy when systems 1 and 2 are put in direct contact, then a process takes place, so that the transitivity property for the equilibrium apparently does not hold. Work is in progress in

order to clarify this point.

We finally mention some other approaches to the foundations of statistical thermodynamics which share some similarities with ours. The relevance of correlation functions in nonequilibrium situations was particularly stressed by Zubarev (see the book [17] and an example of application given in [18]). One has then the well-known Ruelle's principle (see [19]), which is mostly concerned with the form of the stationary measures, particularly developed by Gallavotti and Cohen [20]. In this connection, see also [21, 22] and, for a recent work using stochastic dynamics, the already quoted paper [13].

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