Work, dissipation, and fluctuations in nonequilibrium physics

Short-time fluctuations of displacements and work

Ramses van Zon [a,c,*], S.S. Ashwin [b,c], E.G.D. Cohen [c]

[a] *Chemical Physics Theory Group, Department of Chemistry, University of Toronto, 80, Saint George Street, Toronto, Ontario M5S 1A1, Canada*
[b] *Department of Chemistry, University of Saskatchewan, 110, Science Place, Saskatoon, Saskatchewan S7N 5C9, Canada*
[c] *The Rockefeller University, 1280 York Avenue, New York, NY 10021-6399, USA*

Abstract

A recent theorem giving the initial behavior of very short-time fluctuations of particle displacements in classical many-body systems is discussed. It has applications to equilibrium and non-equilibrium systems, one of which is a series expansion of the distribution of work fluctuations around a Gaussian function. To determine the time-scale at which this series expansion is valid, we present preliminary numerical results for a Lennard-Jones fluid. These results suggest that the series expansion is useful up to time scales on the order of a picosecond, below which a simple Gaussian function for the distribution of the displacements can be used. ***To cite this article: R. van Zon et al., C. R. Physique 8 (2007).***
© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Résumé

Fluctuations aux temps courts des déplacements et du travail. Un théorème récent est discuté qui donne le comportement initial des fluctuations aux temps très courts des déplacements de particules dans les systèmes classiques à plusieurs corps. Il a des applications dans les systèmes à l'équilibre et hors d'équilibre, dont l'une est un développement en série de la distribution des fluctuations du travail autour d'une fonction gaussienne. Pour déterminer l'échelle de temps sur laquelle ce développement en série est valable, nous présentons des résultats numériques préliminaires pour le fluide de Lennard-Jones. Ces résultats suggèrent que le développement en série est utile jusqu'à une échelle de temps de l'ordre de la picoseconde, pendant laquelle une simple fonction gaussienne des déplacements peut être utilisée. ***Pour citer cet article : R. van Zon et al., C. R. Physique 8 (2007).***
© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

* Corresponding author at: Chemical Physics Theory Group, Department of Chemistry, University of Toronto, 80, Saint George Street, Toronto, Ontario M5S 1A1, Canada.
E-mail address: rzon@chem.utoronto.ca (R. van Zon).

1. Introduction

In recent years, non-equilibrium fluctuations in entropy production, work and heat have become the subject of intense study. In this context, results such as the stationary state fluctuation theorem [1] have given a deeper insight in the behavior and character of non-equilibrium systems beyond irreversible thermodynamics and hydrodynamics, which are especially important for small systems such as biomolecules and nanotechnology.

The fluctuation theorem of a non-equilibrium steady state considers fluctuations at long time-scales. Fluctuations of work, heat and entropy production at *short* time-scales are however less often studied. Such fluctuations play a role in short-time (picosecond) non-equilibrium transport at the nanometer scale such as in incoherent neutron scattering, among others. While fluctuations of many properties can be studied, the present article will give an overview of recent results for short-time fluctuations of the displacements of individual particles in a classical-mechanical system. In particular, we will focus on a theorem regarding the probability distribution of the short-time fluctuations of displacements [2,3]. As we will show in this paper, this distribution is also related to that of work fluctuations. Furthermore, we will discuss its implications and range of applicability.

The paper is structured as follows: in Section 2 we introduce moments and cumulants of a probability distribution, in terms of which the theorem is formulated. In Section 3 we give a simple example of the short-time behavior of cumulants as a prelude to the theorem presented in Section 4. One equilibrium and one non-equilibrium application of this theorem are discussed in Section 5. Preliminary results on the range of validity of the short-time expansion and thus of the utility of the theorem are presented in Section 6. We end with the conclusions in Section 7.

2. Moments and cumulants

Consider a classical system of N particles with positions $\boldsymbol{r}_i$ and velocities $\boldsymbol{v}_i$. The equations of motions are Hamiltonian with forces derived from a smooth potential $U(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$, while the initial phase points have a probability distribution denoted by $\rho(\{\boldsymbol{r}_i, \boldsymbol{v}_i\})$. In the current context, Lennard-Jones potentials may be considered smooth, despite the singularity at zero, provided initial conditions which hit this singularity have measure zero.

In time, the particles will be displaced from their initial position by an amount

$$\Delta \boldsymbol{r}_i(t) = \boldsymbol{r}_i(t) - \boldsymbol{r}_i(0) = \left(\Delta x_i(t), \Delta y_i(t), \Delta z_i(t) \right)$$

The probability distribution of these displacements, $P(\Delta \boldsymbol{r}_1, \ldots, \Delta \boldsymbol{r}_N, t)$, is determined by the dynamics and the initial probability distribution.

Instead of considering the probability distribution function $P(\Delta \boldsymbol{r}_1, \ldots, \Delta \boldsymbol{r}_N, t)$ itself, it is often useful to consider the moments of this distribution which are defined as

$$\mu_{\boldsymbol{n}_1 \ldots \boldsymbol{n}_N}(t) = \left\langle \Delta x_1^{n_{1x}} \Delta y_1^{n_{1y}} \Delta z_1^{n_{1z}} \cdots \Delta x_N^{n_{Nx}} \Delta y_N^{n_{Ny}} \Delta z_N^{n_{Nz}} \right\rangle_t \tag{1}$$

where the average $\langle \rangle_t$ is taken with $P(\Delta \boldsymbol{r}_1, \ldots, \Delta \boldsymbol{r}_N, t)$ and each $\boldsymbol{n}_i$ is triplet of integers, $\boldsymbol{n}_i = (n_{ix}, n_{iy}, n_{iz})$. These moments determine the moment generating function

$$\hat{P}(\boldsymbol{k}_1, \ldots, \boldsymbol{k}_N, t) = \sum_{n_{1x}=0}^{\infty} \frac{(ik_{1x})^{n_{1x}}}{n_{1x}!} \sum_{n_{1y}=0}^{\infty} \frac{(ik_{1y})^{n_{1y}}}{n_{1y}!} \sum_{n_{1z}=0}^{\infty} \frac{(ik_{1z})^{n_{1z}}}{n_{1z}!} \cdots \sum_{n_{Nz}=0}^{\infty} \frac{(ik_{Nz})^{n_{Nz}}}{n_{Nz}!} \mu_{\boldsymbol{n}_1 \cdots \boldsymbol{n}_N}(t) \tag{2}$$

which coincides with the Fourier transform of $P(\Delta \boldsymbol{r}_1, \ldots, \Delta \boldsymbol{r}_N, t)$. Thus all information about $P(\Delta \boldsymbol{r}_1, \ldots, \Delta \boldsymbol{r}_N, t)$ is in principle contained in these moments.

A special case is formed by taking $\boldsymbol{n}_1 = (n, 0, 0)$ and all other $\boldsymbol{n}_{i \neq 1} = 0$, which means one considers the distribution of the displacement of a single particle, $P(\Delta x, t)$. Its moments are given by $\mu_n(t) = \langle \Delta x_1^n \rangle_t$ and its generating function by

$$\hat{P}(k, t) = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \mu_n(t) = \left\langle \exp(ik \Delta x) \right\rangle_t$$

In equilibrium, $\hat{P}(k, t)$ becomes equal to the incoherent intermediate scattering function that can be measured e.g. by neutron scattering.

In special cases, such as for an ideal gas or a harmonic lattice in equilibrium, the moment generating function is Gaussian and then determined by the first and second moments, i.e. for the single particle displacement by the $\mu_1(t)$ and $\mu_2(t)$. Even in those cases, the higher order moments are not zero, but can be expressed as simple factored forms involving $\mu_1(t)$ and $\mu_2(t)$ only, e.g., $\mu_3(t) = 3\mu_1(t)\mu_2(t) - 2\mu_1^3(t)$ and $\mu_4(t) = 3\mu_2^2(t) - 2\mu_1^4(t)$.

A more convenient representation of the distribution for Gaussian and near-Gaussian distributions is in terms of cumulants, which are, loosely stated, moments with all possible factorizations taken out. Formally, they are defined as the derivatives of the logarithm of $\hat{P}$, such that:

$$\sum_{n=1}^{\infty} \frac{(ik)^n}{n!} \kappa_n(t) = \log \hat{P}(k, t) \tag{3}$$

This equation defines the cumulants $\kappa_n(t)$ for the single particle displacement distribution $P(\Delta x, t)$, but it can easily be generalized to deal with the general case of $P(\Delta r_1, \ldots, \Delta r_N, t)$. Note that in case of a Gaussian distribution, the cumulants κ_n with $n > 2$ are all equal to zero.

One can find explicit expressions for the cumulants by substituting the expression on the right-hand side of Eq. (2) into the right-hand side of Eq. (3), expanding the logarithm and equating terms of equal powers in k. For the first four powers of k this yields

$$\kappa_1(t) = \mu_1(t) \tag{4a}$$

$$\kappa_2(t) = \mu_2(t) - \mu_1^2(t) \tag{4b}$$

$$\kappa_3(t) = \mu_3(t) - 3\mu_1(t)\mu_2(t) + 2\mu_1^3(t) \tag{4c}$$

$$\kappa_4(t) = \mu_4(t) - 4\mu_1(t)\mu_3(t) - 3\mu_2^2(t) + 12\mu_1^2(t)\mu_2(t) - 6\mu_1^4(t) \tag{4d}$$

These first four cumulants are also known as the mean, variance, skewness and kurtosis, respectively. As expected, using the relations between the moments of a Gaussian distribution given above, one gets $\kappa_3(t) = \kappa_4(t) = 0$. Thus if one finds $\kappa_3(t)$ or $\kappa_4(t)$ (or in fact any $\kappa_{n>2}$) is nonzero, this is a sign that the distribution is not Gaussian.

3. Short-time behavior: a harmonic example

As an illustrative example, consider a single particle of mass one in one dimension, subject to a harmonic potential $U = x^2/2$. Let the initial velocity distribution be Gaussian:

$$\rho(v_0) = (2\pi k_B T)^{-1/2} \exp\left[-\frac{v_0^2}{2k_B T}\right] \tag{5}$$

The distribution of the initial positions x_0 will be arbitrary and given by some function $p(x_0)$. Because p is arbitrary, this single-particle system is not necessarily in equilibrium.

The equations of motion of this system are easily solved and give

$$x(t) = \cos t\, x_0 + \sin t\, v_0 \tag{6}$$

Using Eqs. (5) and (6), the function $\hat{P}(k, t)$, i.e., the Fourier transform of $P(\Delta x, t)$ with $\Delta x = x(t) - x_0$, can now be computed:

$$\begin{aligned}
\hat{P}(k, t) &= \int dx_0 \int dv_0\, p(x_0)\rho(v_0) e^{ik[x(t)-x_0]} \\
&= \int dx_0 \int dv_0\, p(x_0)\rho(v_0) e^{ik[(\cos t-1)x_0 + \sin t\, v_0]} \\
&= \int dx_0\, p(x_0) e^{ik(\cos t-1)x_0} \int dv_0\, \rho(v_0) e^{ik \sin t\, v_0} \\
&= \hat{p}(k[\cos t - 1]) \exp\left[-\frac{k^2}{2} k_B T \sin^2 t\right]
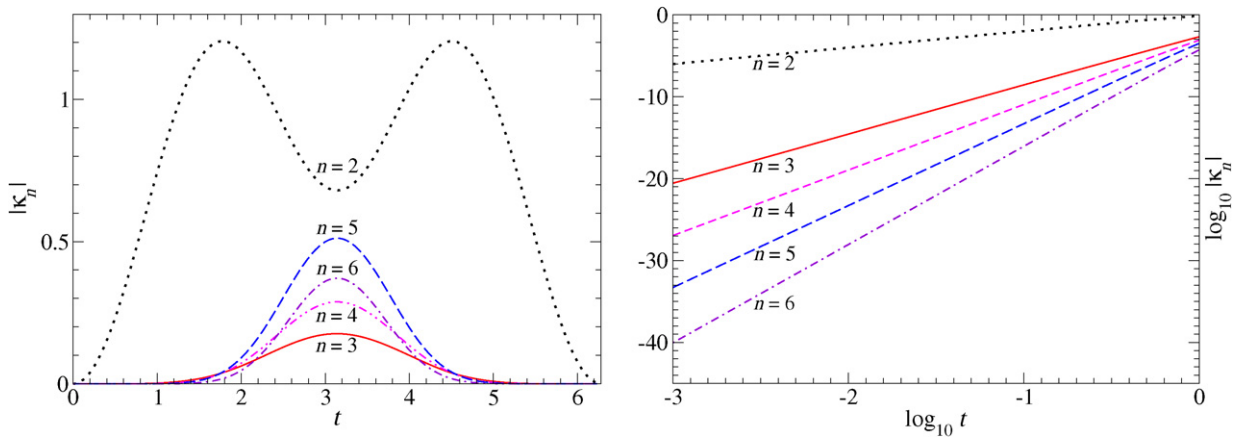\end{aligned} \tag{7}$$

Fig. 1. Short-time behavior of cumulants of the displacement of a particle in a harmonic potential, initially not in equilibrium, based on Eq. (8). The left plot shows the cumulants κ_n as a function of time t, for $n = 2, 3, 4, 5$ and 6, respectively. The right plot shows the same on a log-log scale, to bring out the scaling behavior for small t.

where $\hat{p}$ is the Fourier transform of the distribution of initial positions, $p(x_0)$. Given this result for $\hat{P}(k, t)$ and Eq. (3), one finds for the cumulants:

$$\kappa_n(t) = \kappa_n^{(0)}(\cos t - 1)^n + \delta_{n,2} k_B T \sin^2 t \tag{8}$$

where $\kappa_n^{(0)}$ is the nth cumulant of $p(x_0)$.

An example of the cumulant behavior in Eq. (8) is given in Fig. 1. For this example, we chose $k_B T = 1$ and for $p(x_0)$ a non-Gaussian function which is continuous and piece-wise linear:

$$p(x_0) = \begin{cases} \dfrac{3}{4}(1 + x_0) & \text{if } -1 < x_0 < \dfrac{1}{3} \\ \dfrac{3}{2}(1 - x_0) & \text{if } \dfrac{1}{3} < x_0 < 1 \\ 0 & \text{otherwise} \end{cases}$$

The reason for choosing this $p(x_0)$ is that its cumulants are non-trivial yet easy to compute. The first panel in Fig. 1 shows the behavior of the cumulants κ_n for $n = 2, 3, 4, 5$ and 6 as a function of time. The second panel shows the same quantities, but zooms in on the small time behavior and has a log-log scale. On this log-log scale, the curves for $n = 2, 3, 4, 5$ and 6 have, for small t, slopes $-2, -6, -8, -10$ and -12, respectively. This means that for small t, $\kappa_2 \propto t^2$, while $\kappa_{2 < n \leqslant 6} \propto t^{2n}$. It can easily be verified that Eq. (8) supports this observation for all choices of $p(x_0)$ and for all $n > 2$.

One may wonder whether the t^{2n} behavior of $\kappa_n(t)$ for small times t is general, or whether it is due to the simplicity of our example. In fact, this behavior is more general, under conditions explained in the next section.

4. Theorem on short-time fluctuations of displacements

Cumulants of particle displacements have been studied in the context of the intermediate scattering function in the field of neutron scattering on equilibrium systems for a long time [4–6]. It was found that while all odd cumulants of displacements are zero in equilibrium, the even cumulants for small times obey $\kappa_n(t) \propto |t|^{n+1}$ for hard spheres [6], while for systems with smooth potentials it was known that $\kappa_4(t) \propto t^8$ [4] and $\kappa_6(t) \propto t^{12}$ [5].

Unfortunately, these results for smooth potentials only held for equilibrium systems and furthermore no results for general n were available. A recent theorem however, generalizes these results to certain non-equilibrium systems and to general n [2,3]. It states that if

(i)　the forces are smooth functions of the positions of the particles (smooth here means that all derivatives exist for all points in phase space except a set of measure zero),

(ii) the forces are independent of the velocities,
(iii) the initial velocities are Gaussian distributed, and
(iv) the initial velocities are independent of the initial positions,

then the cumulants of particle displacements satisfy for small times t

$$\kappa_n(t) = \begin{cases} c_n t^n + \mathcal{O}(t^{n+1}) & \text{for } n < 3 \\ c_n t^{2n} + \mathcal{O}(t^{2n+1}) & \text{for } n \geqslant 3 \end{cases} \tag{9}$$

where the c_n are constants. In fact, all n-order cumulants satisfy this rule (an n-order cumulant is cumulant $\kappa_{\boldsymbol{n}_1 \cdots \boldsymbol{n}_N}$ such that $\sum_i (n_{ix} + n_{iy} + n_{iz}) = n$).

We stress that this theorem applies to non-equilibrium as well as to equilibrium systems, because the (initial) position distribution can be arbitrary and does not have to be equal to its equilibrium form. A common class of non-equilibrium systems covered by the theorem consists of those that start out in equilibrium and are then driven out of equilibrium by some external perturbation, because the requirement of a Gaussian velocity distribution only has to be satisfied at the initial time.

A sketch of the proof of this theorem was given in Ref. [2], while the full proof can be found in Ref. [3]; we will therefore not prove the theorem again here. However, we do want to remark that the nature of the dynamics is largely unimportant for the theorem to hold (as long as the forces are smooth), and that the most important requirement seems to be that the velocities are initially Gaussian distributed. To what extent one can relax the requirement that this Gaussian distribution be independent of the initial positions, is at present not clear.

5. Applications

5.1. Neutron scattering in equilibrium systems

As mentioned above, the short time behavior of the cumulants of displacement arises in the context of neutron scattering. In fact, in equilibrium, the incoherent structure function $F_s(k, t)$ is precisely the Fourier transform of the distribution of single particle displacements $\hat{P}(k, t)$ [7]. Given Eq. (3), we can therefore write

$$F_s(k, t) = \exp\left[\sum_{n=2}^{\infty} \frac{\kappa_n(t)}{n!} (ik)^n \right] \tag{10}$$

Note that all odd cumulants are zero for an equilibrium system for symmetry reasons.

For small wave-vector k, the terms involving higher cumulants in Eq. (10) can be neglected and $F_s(k, t)$ becomes approximately Gaussian, as does its Fourier inverse, the Van Hove self-correlation function $G_s(\Delta x, t)$. While Eq. (10) in principle allows for a systematic improvement on this Gaussian approximation by increasing the number of terms considered in the cumulant sum, in its current form, it is not possible to take into account higher order cumulants and still perform the Fourier inverse analytically. To obtain a systematic analytic improvement upon the Gaussian approximation of the Van Hove self-correlation function one first has to expand the right-hand side of Eq. (10) around a Gaussian as follows:

$$F_s(k, t) = \exp\left[-\frac{1}{2}\kappa_2(t)k^2 \right]\left[1 + \frac{\kappa_4(t)}{4!}k^4 - \frac{\kappa_6(t)}{6!}k^6 + \cdots \right] \tag{11}$$

By taking the Fourier inverse of this expression, we find for the Van Hove self-correlation function

$$G_s(\Delta x, t) = \frac{\exp(-w^2)}{\sqrt{2\pi\kappa_2(t)}}\left[1 + \frac{\kappa_4(t)H_4(w)}{4!4\kappa_2^2(t)} + \frac{\kappa_6(t)H_6(w)}{6!8\kappa_2^3(t)} + \cdots \right] \tag{12}$$

where $w = \Delta x/\sqrt{2\kappa_2}$ and H_n is the nth Hermite polynomial.

Provided that the system has smooth forces independent of the velocities (conditions 1 and 2 of the theorem, respectively), the third and fourth conditions are automatically satisfied in (canonical) equilibrium. The application of the theorem now consists of noting that, with $w = \mathcal{O}(1)$, the terms inside the brackets on the right-hand side of Eq. (12) are 1, t^4, t^6, respectively. It can be shown that this behavior persists, i.e., each next term is two powers

of t higher than the previous one. Hence as a consequence of the theorem, the subsequent terms in this expansion become successively smaller if t is small, so that a truncation of the expansion can give an accurate approximation to $G_s(\Delta x, t)$.

5.2. Distribution of work done by an external field

Since the theorem is not restricted to equilibrium systems, we want to discuss at least one interesting application of the theorem to a non-equilibrium system, namely a system in a constant external field along the positive x direction. This constant external field exerts a constant force $\boldsymbol{F}$ on all N particles, which does an amount of work W on the system. Since the initial conditions are drawn from a probability distribution, W will be a fluctuating quantity. Non-equilibrium fluctuations of work have been investigated in the context of the fluctuation theorem [1] and the non-equilibrium work relation [8]. The theorem of Section 4 can be used to investigate a different aspect of the work fluctuations, namely their very short-time behavior.

Consider now the work W done on the system by this force during a time t:

$$W = \sum_{i=1}^{N} \int_{0}^{t} dt' \, \boldsymbol{F} \cdot \boldsymbol{v}_i(t') = |\boldsymbol{F}| \sum_{i=1}^{N} \Delta x_i(t)$$

Given this linear relation between the displacements and the work, the short-time theorem can be applied to the distribution of work values as well. To see this, one can apply the multinomial expansion [3] to the nth cumulants of the work distribution, i.e.

$$\kappa_n^W(t) = \sum_{\sum_{j=1}^{N} n_j = n} \frac{n!}{n_1! n_2! \dots n_N!} \kappa_{n_1 n_2 \dots n_N}(t) \tag{13}$$

where $\kappa_{n_1 n_2 \dots n_N} = \kappa_{\boldsymbol{n}_1 \boldsymbol{n}_2 \dots \boldsymbol{n}_N}$ with $\boldsymbol{n}_j = (n_j, 0, 0)$. Examples are $\kappa_1^W = N\kappa_{100\dots}$ and $\kappa_2^W = N\kappa_{200\dots} + N(N-1)\kappa_{1100\dots}$ (where we used that the particle are indistinguishable). If the forces are smooth and independent of the particles' velocities and if the initial velocities of the particles are Gaussian distributed, then according to the theorem, each term in the sum on the right-hand side of Eq. (13) is of order t^{2n} if $n > 2$. In other words, the nth cumulant of the work fluctuations $\kappa_n^W(t)$ also scales as t^{2n} for $n > 2$ if t is small enough. Consequently, the distribution of work fluctuations may be written in a similar expansion as that of the Van Hove self-correlation function in Eq. (12).

6. Relevant time scale for an equilibrium Lennard-Jones fluid

We have discussed the short-time behavior of the cumulants of displacements, but we have not yet addressed the question of how short the time scale has to be for the above applications to be meaningful. We will now address this question now for single particle displacements, which play a significant role in the Van Hove self-correlation function G_s. We would call the series expansion of G_s in Eq. (12) meaningful if each next term is smaller than the previous one. While the theorem guarantees that this is so below some time-scale, it does not say what this time scale is. An estimate for the time scale at which these short-time results will no longer be applicable could be found by considering the time $t = \tau_G$ at which the first correction term in Eq. (12) becomes of comparable magnitude as the first term (the Gaussian). In that case, the series in Eq. (12) can no longer be expected to be useful. Note that in Eq. (12) all odd cumulants have vanished because of time-reversal symmetry, so the first correction term involves κ_2 and κ_4, or, using Eq. (9), the values of the constants c_2 and c_4. Since $w = \mathcal{O}(1)$, one can find τ_G by equating the first and (the absolute value of) the second term in Eq. (12) with t set to τ_G and $H(w)$ set to 1:

$$1 = \left| \frac{c_4 \tau_G^8}{4!4[c_2 \tau_G^2]^2} \right|$$

where Eq. (9) was used. Solving this equation for τ_G yields
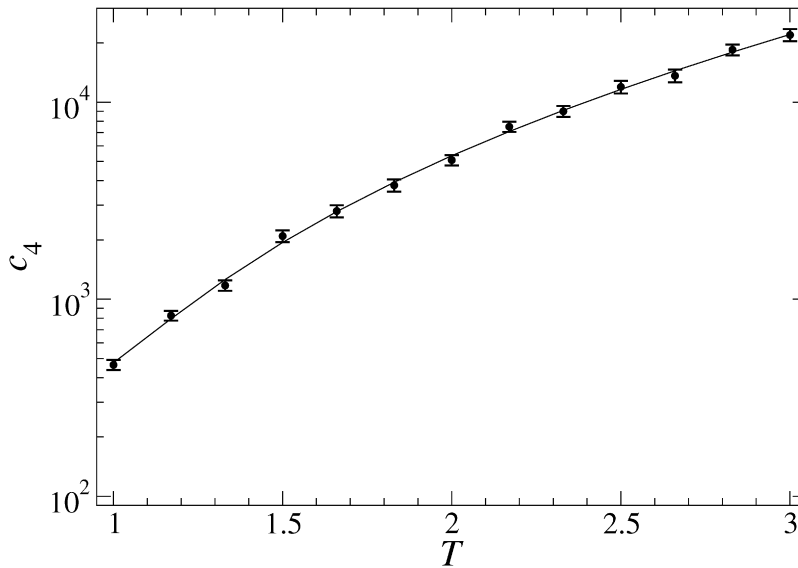
$$\tau_G = \left(\frac{96 c_2^2}{|c_4|} \right)^{1/4} \tag{14}$$

Fig. 2. Numerical results for c_4, the coefficient in front of the t^8 behavior of κ_4, as a function of the kinetic temperature T. The horizontal lines through the points are the error-bars. The system is a Lennard-Jones fluid with density $\rho = 0.8$. These results are from a MD simulation in an NVE ensemble with $N = 100$ particles, with periodic boundary conditions. All quantities are in LJ units.

Expression for c_n can be found in Section 3.4 of Ref. [3]. While the values of the c_n will be system dependent, but it is nonetheless of interest to have a realistic estimate of τ_G. For this purpose, we performed molecular dynamics (MD) simulations at constant volume and energy (NVE) for an equilibrium $N = 100$ particle system with periodic boundary conditions [9]. The inter-atomic potential used is the Lennard-Jones (LJ) potential $V(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. All quantities reported are in Lennard-Jones units: length in units of σ, temperature in units of ε/k_B, number density (ρ) in units of σ^{-3} and time in units of $\tau_{LJ} = (\sigma^2 m/\varepsilon)^{1/2}$, where m is the mass of the particle. Since these are arbitrary units, to understand the physical consequences of our results, we use the LJ parameters of a specific substance as a reference, namely Argon. In that case, τ_{LJ} corresponds to 2.16 picoseconds while $\varepsilon/k_B = 119.8$ K [9]. In the simulation, a potential cutoff of $r_c = 2.5\sigma$ was used and the equations of motion were integrated using the Verlet algorithm [9] with a time step of one femtosecond. Data were accumulated once equilibrium had been attained in the simulation and collected between sufficiently long periodic time intervals, in order to ensure statistically uncorrelated data points.

Note that while strictly the theorem should be applied to a system in the canonical (NVT) ensemble (to ensure a Gaussian velocity distribution), the preliminary data presented here are obtained in the microcanonical ensemble (NVE). Since in the thermodynamic limit, these two ensemble should become equivalent, the time scale τ_G obtained in the NVE simulation is expected to be very close to the τ_G that would be found in an NVT simulation.

In Fig. 2, we show preliminary results from these simulations for c_4 as a function of the kinetic temperature T. More results will appear in Ref. [10]. The value of $c_2 = k_B T$, so from the results in Fig. 2 we can estimate the time scale τ_G using Eq. (14). It is found that this time scale ranges from $\tau_G = 0.5$ for $T = 1$ to $\tau_G = 5$ for $T = 3$, all in Lennard-Jones units. This corresponds to time scales on the order of 1 picoseconds for $T = 119.8$ K to 10 picoseconds for $T = 359.4$ K. We note that these time scales are to be interpreted as upper bounds on the times at which expansions such as those in Eq. (12) break down.

7. Conclusions

We discussed a recent theorem which states that for smooth systems with initial Gaussian velocity distributions (but with arbitrary position distributions), the cumulants satisfy a scaling relation for short times: $\kappa_n \propto t^n$ if $n < 3$ and $\kappa_n \propto t^{2n}$ for $n \geqslant 3$. As applications of this theorem, this scaling implies that the expansion of the Van Hove self-correlation function around a Gaussian is useful, as is a similar expansion for the short-time work fluctuations in a non-equilibrium system subject to a constant external field (provided the initial distribution of velocities is Gaussian).

We also showed some preliminary numerical results for a Lennard-Jones model of Argon which suggest that this expansion breaks down for larger times, with an upper limit of 0.6 to 6 ps depending on the kinetic temperature. Further details will be published in a later paper [10].

Finally, we wish to note that other applications of the theorem are the scaling of non-Gaussian parameters characterizing 'dynamical heterogeneities' in supercooled liquids and glasses, and non-equilibrium transport using a Green's functions approach; see Ref. [3] for details.

Acknowledgements

References

[1] D.J. Evans, E.G.D. Cohen, G.P. Morriss, Phys. Rev. Lett. 71 (1993) 2401;
    G. Gallavotti, E.G.D. Cohen, Phys. Rev. Lett. 74 (1995) 2694.
[2] R. van Zon, E.G.D. Cohen, Physica A 365 (2006) 108.
[3] R. van Zon, E.G.D. Cohen, J. Stat. Phys. 123 (2006) 1.
[4] P. Schofield, in: Inelastic Scattering of Neutrons in Solids and Liquids, IAEA, Vienna, 1961, p. 39.
[5] V.F. Sears, Phys. Rev. A 5 (1972) 452.
[6] I.M. de Schepper, M.H. Ernst, E.G.D. Cohen, J. Stat. Phys. 25 (1981) 321.
[7] J.-P. Hansen, I.R. McDonald, Theory of Simple Liquids, Academic Press, London, 1986.
[8] C. Jarzynski, J. Stat. Mech. (2004) P09005;
    See also E.G.D. Cohen, D. Mauzerall, J. Stat. Mech. (2004) P07006.
[9] D. Frenkel, B. Smit, Understanding Molecular Simulation, Academic Press, San Diego, 1996.
[10] S.S. Ashwin, R. van Zon, E.G.D. Cohen, Numerical investigation into single particle correlations on picosecond and sub-picosecond time scales in Lennard-Jones fluids, in preparation.