

Theorem on the distribution of short time single particle displacements

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Abstract

The distribution of the initial very short-time displacements of a single particle is considered for a class of classical systems with Gaussian initial velocity distributions and arbitrary initial particle positions. A very brief sketch is given of a rather intricate and lengthy proof that for this class of systems the n th order cumulants behave as t^{2n} for all $n > 2$, rather than as t^n . We also briefly discuss some physical consequences for liquids.

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1. Introduction

This paper is meant to give a pedagogical sketch of the proof of a theorem for the distribution of initial very short time single particle displacements in terms of cumulants for a class of classical systems with smooth potentials, which can be in or out of equilibrium. This theorem is based on a time expansion around $t = 0$.

The theorem has a number of physical applications [1], including incoherent neutron scattering in equilibrium systems [2,3], heterogeneous dynamics in supercooled glass-formers [4] and the recently developed Green's function approach to transport on picosecond time scales, when the system is far from equilibrium [5,6].

In order to formulate the theorems we first introduce the moments and cumulants of the distribution of single particle displacements.

2. Moments and cumulants

In a classical system of N particles with positions \mathbf{r}_i and velocities \mathbf{v}_i , we can consider the displacement $\Delta\mathbf{r}_i(t) = \mathbf{r}_i(t) - \mathbf{r}_i(0)$ of an individual particle i in a time t . For simplicity, we will only consider here the displacement $\Delta x_1(t) = \Delta\mathbf{r}_1(t) \cdot \hat{\mathbf{x}}$ of particle 1 in the x direction.

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Given the time t and an initial point in phase space, $\Delta x_1(t)$ is unique. However, we will consider an ensemble of initial conditions, so that each initial point has a certain probability associated with it. In fact, the theorem discussed here is applicable to systems whose initial phase space distribution is of the form

$$P(\mathbf{r}^N, \mathbf{v}^N) = f(\mathbf{r}^N) \prod_{i=1}^N \left(\frac{\beta_i m_i}{2\pi} \right)^{3/2} \exp \left[-\frac{1}{2} \beta_i m_i |\mathbf{v}_i - \mathbf{u}_i|^2 \right]. \quad (1)$$

Here \mathbf{r}^N and \mathbf{v}^N represent the collection of the coordinates $\mathbf{r}^N \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ and the velocities $\mathbf{v}^N \equiv (\mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_N)$ of all N particles in the system, respectively, $\mathbf{u}_i = \langle \mathbf{v}_i \rangle_{t=0}$ for each particle $i = 1, 2, \dots, N$ and $f(\mathbf{r}^N)$ is a well behaved, i.e., normalized, but otherwise arbitrary probability distribution function of the \mathbf{r}^N at $t = 0$.¹ We will take $\mathbf{u}_i = 0$ in the following for simplicity.

Because of the ensemble distribution of initial phase space points, $\Delta x_1(t)$ is not fixed but has a probability distribution. To characterize this probability distribution function, one may determine its moments

$$\mu_n(t) = \langle [\Delta x_1(t)]^n \rangle. \quad (2)$$

The first moment ($n = 1$) is the average of $\Delta x_1(t)$, the second moment is the average of its square, etc. It may be noted that for small times t , $\Delta x_1(t) \approx v_{1x}t$, whence one expects

$$\mu_n(t) \propto t^n. \quad (3)$$

The moments may alternatively be calculated from $\mu_n(t) = \partial^n F_s(k, t) / \partial (ik)^n |_{k=0}$ using the moment generating function

$$F_s(k, t) = \sum_{n=0}^{\infty} \mu_n(t) \frac{(ik)^n}{n!} \quad (4)$$

$$= \langle e^{ik\Delta x_1(t)} \rangle. \quad (5)$$

Here we used Eq. (2) in the last equality. The quantity on the right-hand side of Eq. (5) is precisely the self-part of the intermediate scattering function (the Fourier transform of the Van Hove self-correlation function) and can be measured through incoherent neutron scattering [2]. Note that we need in principle all $\mu_n(t)$ for n from zero to infinity to find $F_s(k, t)$.

Sometimes however, it is known that the first two moments suffice, namely for an ideal gas and for a perfectly harmonic system, in which cases F_s and the Van Hove self-correlation function are Gaussian. This may still be approximately true in less ideal situations, and in fact, for short times (such as the ones that we are interested in here) one expects the system to behave almost like an ideal gas. So it makes sense to try to expand around a Gaussian as a zeroth order approximation.

In such near-Gaussian cases, the so-called cumulants κ_n are a more convenient set of parameters to work with than the moments [7]. The cumulants can be found from the cumulant generating function $\log F_s(k, t)$, i.e.,

$$\kappa_n(t) = \frac{\partial^n}{\partial (ik)^n} \log F_s(k, t) |_{k=0} \quad (6)$$

so that

$$F_s(k, t) = \exp \left[\sum_{n=1}^{\infty} \kappa_n(t) \frac{(ik)^n}{n!} \right]. \quad (7)$$

Here we will write for convenience the n th cumulant $\kappa_n(t) \equiv \langle \langle \Delta x_1^{[n]} \rangle \rangle$, and stress that $[n]$ is not a power but an index indicating the order of the derivative of the generating function; for $n = 1$ the superscript will be omitted. Equating the right-hand sides of Eqs. (4) and (7), one can derive the first few cumulants in terms of the moments:

$$\kappa_1(t) = \mu_1(t),$$

¹In Eq. (1) a multi-component mixture would have different m_i for particles i , depending on to which component they belong, while β_i allows the particle to belong to a component with a different temperature at $t = 0$ than other particles may have.

$$\kappa_2(t) = \mu_2(t) - \mu_1^2(t),$$

$$\kappa_3(t) = \mu_3(t) - 3\mu_2(t)\mu_1(t) + 2\mu_1^3(t), \quad \text{etc.} \quad (8)$$

In general $\kappa_n(t)$ is composed of products of moments of degree m , by dividing its index n in all possible ways into a sum of integers $m \leq n$, so that their sum m equals n . From Eq. (3), one would then expect:

$$\kappa_n(t) \propto t^n. \quad (9)$$

3. The theorem

Schofield [8] and Sears [9] found by straightforward but complicated calculations for the initial short time behavior of the $\kappa_n(t)$ the following results in equilibrium (where all odd indexed cumulants vanish):

$$\kappa_2(t) = \mathcal{O}(t^2), \quad \kappa_4(t) = \mathcal{O}(t^8), \quad \kappa_6(t) = \mathcal{O}(t^{12}) \quad (10)$$

instead of the expected behavior $\kappa_n(t) = \mathcal{O}(t^n)$ suggested by Eq. (9).

Our theorem is a generalization of Schofield and Sears' suggestive results for the first three non-vanishing cumulants for neutron scatterings in equilibrium to the general class of systems, characterized by the initial distribution function (1).

The theorem states that if (a) the interparticle and external forces on the particles are smooth and independent of their velocities, and (b) the velocities are Gaussian distributed and independent of the initial \mathbf{r}^N at $t = 0$, then

$$\kappa_n(t) = \begin{cases} c_n t^n + \mathcal{O}(t^{n+1}) & \text{for } n \leq 2, \\ c_n t^{2n} + \mathcal{O}(t^{2n+1}) & \text{for } n > 2, \end{cases} \quad (11)$$

where the c_n depend on the forces but not on t .

This result (11) implies hidden correlations in the moments $\mu_n(t)$, which are not eliminated by the simple moment expansion (8) of the cumulants $\kappa_n(t)$.

4. Sketch of proof of theorem

The proof of the theorem (11) proceeds as follows, where we give only some of the most important steps. The full proof is presented in Ref. [1].

1. We consider systems of N particles $i = 1, \dots, N$ in $d = 3$ with $\mathcal{N} = 3N$ degrees of freedom. It is convenient for the formulation of the proof to associate with each degree of freedom of the particles i , (generalized) positions r_i and velocities v_i respectively, but now with $i = 1, \dots, \mathcal{N}$. Thus, $r_{1x} \rightarrow r_1, r_{1y} \rightarrow r_2, r_{1z} \rightarrow r_3, v_{1x} = v_1, \dots$, transforming $\mathbf{r}^N, \mathbf{v}^N$ to $r^{\mathcal{N}}, v^{\mathcal{N}}$. The equations of motion are then for $i = 1, \dots, \mathcal{N}$:

$$\dot{r}_i = v_i, \quad \dot{v}_i = F_i(r^{\mathcal{N}}, t)/m_i = a_i(r^{\mathcal{N}}, t). \quad (12)$$

2. Expand $\Delta r_1(t)$ in powers of t around $t = 0$

$$\Delta r_1(t) = \sum_{m=1}^{\infty} \frac{t^m}{m!} \left. \frac{d^m \Delta r_1(t)}{dt^m} \right|_{t=0}. \quad (13)$$

3. Here the coefficients of t^m are polynomials in v_1 :

$$P_1 \equiv \frac{d\Delta r_1(t)}{dt} = v_1,$$

$$P_2 \equiv \frac{d^2 \Delta r_1(t)}{dt^2} = a_1(r^{\mathcal{N}}, t) = \mathcal{O}(1),$$

$$P_3 \equiv \frac{d^3 \Delta r_1(t)}{dt^3} = \frac{\partial a_1}{\partial t} + \sum_{j=1}^{\mathcal{N}} \frac{\partial a_1}{\partial r_j} v_j = \mathcal{O}(v^{\mathcal{N}}),$$

$$P_4 \equiv \frac{d^4 \Delta r_1(t)}{dt^4} = \dots + \sum_{j=1}^{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \frac{\partial^2 a_1}{\partial r_j \partial r_k} v_j v_k = \mathcal{O}((v^{\mathcal{N}})^2) \quad \text{etc.} \quad (14)$$

4. Therefore, the time expansion of $\Delta r_1(t)$ can be written in the form:

$$\Delta r_1(t) = \sum_{j=1}^{\infty} P_j(v^{\mathcal{N}}) t^j = P_1(v^{\mathcal{N}}) t + P_2(v^{\mathcal{N}}) t^2 + \dots + P_n(v^{\mathcal{N}}) t^n + \mathcal{O}(t^{n+1}), \quad (15)$$

where for $j > 1$, P_j is a polynomial of degree $j - 2$ in $v^{\mathcal{N}}$.

5. Then the expansion of $\kappa_n(t)$ up to t^{2n-1} can be written in the form:

$$\kappa_n(t) = \langle\langle \Delta r_1^{[n]}(t) \rangle\rangle = \sum_{\{n_j\}} \frac{n!}{n_1! \dots n_n!} \langle\langle v_1^{[n_1]}; P_2^{[n_2]}(v^{\mathcal{N}}); \dots; P_n^{[n_n]}(v^{\mathcal{N}}) \rangle\rangle t^{\sum_{j=1}^n n_j}, \quad (16)$$

$$\sum_{j=1}^n n_j = n$$

$$\sum_{j=2}^n n_j(j-2) < n_1$$

with a correction of $\mathcal{O}(t^{2n})$. In this equation, the semicolons on the right-hand side of Eq. (16) indicate that the $P_m^{[n]}$ inside the $\langle\langle \dots \rangle\rangle$ are not to be multiplied, since they are elements of a cumulant.

6. One can prove then that all n terms from t^n to t^{2n-1} in the sum in Eq. (16) vanish, so that only the $\mathcal{O}(t^{2n})$ remains and $\kappa_n(t) = \mathcal{O}(t^{2n})$ (for $n > 2$). The proof of this result is based crucially on the Gaussian properties of the velocities, so that $\langle v_i^{2n} \rangle = (2n - 1)!! \langle v_i^2 \rangle^n$ obtains.

The theorem can be generalized to the displacement of a single particle in different directions in a d -dimensional space, as well as to the displacements of different particles, and can also be applied to multi-component mixtures [1].

5. Physical applications

The theorem has a number of physical applications, mostly pertaining to liquids, e.g. (1) It provides a well ordered short time expansion of the Van Hove self-correlation function relevant for incoherent neutron scattering in equilibrium systems [2]; (2) The cumulants are connected to the non-Gaussian parameters α_n introduced by Rahman and Nijboer [3] and which are used as indicators of dynamical heterogeneity in supercooled glass-formers [4]; and (3) It provides a well ordered short time expansion of the Green's functions for far from equilibrium (mass, momentum and energy) transport on the picosecond time scale [5,6]. For a more extensive account of these applications we refer to Ref. [1].

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