Theorem on the Distribution of Short-Time Single Particle Displacements with Physical Applications

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30 May 2005

Abstract

The distribution of the initial short-time displacements of a single particle is considered for a class of classical systems of particles under rather general conditions. This class of systems contains canonical equilibrium of a multi-component Hamiltonian system as a special case. We prove that for this class of systems the nth order cumulant of the initial short-time displacements behaves as the $2n$-th power of time for all $n > 2$, rather than exhibiting a general nth power scaling. This has direct applications to the initial short-time behavior of the Van Hove self-correlation function, to its non-equilibrium generalizations the Green's functions for mass transport, and to the non-Gaussian parameters used in supercooled liquids and glasses. Moreover, in the context of the Green's functions this theorem is expected to be relevant for mass transport at (sub)picosecond time scales.

KEY WORDS: Single particle diffusion, non-Gaussian effects, cumulants, time expansion, Van Hove self-correlation function, Green's functions, supercooled liquids.

PACS: 05.20.-y, 02.30.Mv, 66.10.-x, 78.70.Nx, 05.60.Cd

1 Introduction

This paper concerns a universal property of correlations of the initial short-time behavior of the displacements of single particles for a rather general class of ensembles of classical systems, both in and out of equilibrium. Among other things, these correlations (expressed in terms of so-called cumulants) have applications to neutron scattering,[1–12] to the description of non-equilibrium systems on picosecond time scales and nanometer length scales[13–17] and to heterogeneous dynamics in supercooled liquids and glasses.[18–22]

Our motivation to consider the displacements of single particles comes from trying to describe the behavior of non-equilibrium systems on all time scales using the so-called Green's function theory. This theory aims to describe, among other things, the time evolution of the number densities, momentum density and energy density, by expressing them in terms of Green's functions. It has so far been successfully applied to self-diffusion[13] and to heat transport[14–16] while a study of mass transport in binary (isotopic) mixtures[17] is in progress. The main advantage of the Green's functions over hydrodynamics is that they can in principle describe the system on all time and length scales, in particular on time scales of the order of picoseconds and on length scales of the order of nanometers. The connection between the picosecond and nanometer scale can be understood by realizing that with typical velocities of 500 m/s, a particle in a fluid at room temperature moves about 0.5 nm in 1 ps. Hence it could also be relevant for nanotechnology, although at present the Green's function theory exists in a classical formulation only and does not yet take quantum-mechanical effects into account.

For mass transport in multi-component fluids,[13, 17] the Green's functions $G_\lambda(r, r', t)$ have the physical interpretation of being the probability that a single particle of component λ is at a position r at time t given that it was at a position r' at time zero. At time zero the system is not in equilibrium, in fact, far-from-equilibrium situations have been studied in this context.[14–17] Given this interpretation, it is clear that the displacements of single particles are the central quantity.

Apart from the non-equilibrium aspect, the above interpretation of the Green's functions is the same as that of the classical equilibrium Van Hove self-correlation function $G_s(r-r', t)$.[1, 8, 9] In the literature on the classical Van Hove self-correlation function in the context of neutron scattering on an equilibrium fluid,[1, 8, 10] it has been noted by Schofield[2] and Sears[7] that the cumulants κ_n (certain combinations of the moments defined below) of the displacement of a particle in a time t in a fluid with a smooth inter-particle potential behave for small t as $\kappa_2 = \mathcal{O}(t^2)$, $\kappa_4 = \mathcal{O}(t^8)$, $\kappa_6 = \mathcal{O}(t^{12})$, while all odd cumulants vanish.

The relevance of the cumulants for the Van Hove self-correlation function can be seen from its Fourier transform, the incoherent intermediate scattering function[1, 8–10]

$$F_s(k, t) = \left\langle e^{\mathrm{i}k\hat{\mathbf{k}}\cdot[\mathbf{r}_1(t)-\mathbf{r}_1(0)]} \right\rangle_{\mathrm{eq}} = \left\langle e^{\mathrm{i}k\Delta x_1(t)} \right\rangle_{\mathrm{eq}}, \tag{1}$$

where k is a wave vector, $\hat{\mathbf{k}}$ its direction (a unit vector), $\mathbf{r}_1(t)$ the position of a (single) particle at time t and $\langle\rangle_{\mathrm{eq}}$ an equilibrium average. In the last equality we have chosen $\hat{\mathbf{k}} = \hat{\mathbf{x}}$ (in an isotropic equilibrium fluid the result is independent of the direction $\hat{\mathbf{k}}$) and defined $\Delta x_1(t)$ as the displacement of the single particle in the x direction: $\Delta x_1(t) = \hat{\mathbf{x}} \cdot [\mathbf{r}_1(t) - \mathbf{r}_1(0)]$. In probability theory[23, 24] $\log\langle\exp[\mathrm{i}kX]\rangle$ is the cumulant generating function for the stochastic variable X, so we see from Eq. (1) that $\log F_s(k,t)$ is the cumulant generating function of $\Delta x_1(t)$. Note that $\Delta x_1(t)$ is a random variable here as it depends on an initial phase point drawn from a probability distribution (here the equilibrium distribution). The cumulant generating function is, by definition, equal to $\sum_{n=1}^{\infty} \kappa_n (\mathrm{i}k)^n/n!$ where κ_n is the nth cumulant.[23, 24] The relation of the incoherent intermediate scattering function and the cumulants of the displacement is thus expressed by[3, 5, 7, 8, 25]

$$F_s(k,t) = \exp \sum_{n=1}^{\infty} \frac{\kappa_n}{n!} (\mathrm{i}k)^n. \tag{2}$$

This connection with the incoherent scattering function (and thus with neutron scattering[1–12]) explains the early interest in the cumulants of displacements from a physical perspective. In section 4 we will discuss also more recent physical applications of the cumulants such as the non-equilibrium Green's functions and non-Gaussian parameters used in the theory of supercooled liquids and glasses.

The results for κ_n mentioned above suggested for equilibrium systems with smooth potentials a behavior as the $2n$-th power in t for κ_n when $n > 2$ but to the best of our knowledge no proof of this property is available at present.

We note that an $\mathcal{O}(t^{2n})$ behavior would be in stark contrast to results obtained for hard disk and hard sphere fluids in equilibrium.[7, 25] Sears[7] considered results up to the 8-th order in t and the 12-th order in t for κ_4 and κ_6, respectively, for smooth potentials and he found by using a limit in which the smooth potential reduces to a hard core potential that for hard spheres $\kappa_4 = \mathcal{O}(|t|^5)$ and $\kappa_6 = \mathcal{O}(|t|^7)$, while the odd cumulants were still zero. An alternative approach was followed by De Schepper *et al.*[25] consisting of directly evaluating the Van Hove self-correlation function for short times for hard spheres based on pseudo-Liouville operators (which replace the usual ones for smooth potentials). De Schepper *et al.*[25] obtained $\kappa_n = \mathcal{O}(|t|^{n+1})$ for all even $n > 2$, with corrections of $\mathcal{O}(|t|^{n+2})$.

The $\mathcal{O}(t^{2n})$ result for smooth potentials is the more remarkable in that a naive estimate of the short time behavior of κ_n based on its connection with the moments would predict a behavior as the n-th order in t. Hence *all* terms from $\mathcal{O}(t^n)$ up to $\mathcal{O}(t^{2n-1})$,[1] should *vanish*. The question we address here is whether this is indeed general for smooth potentials.

[1]Everywhere in this paper 'up to $\mathcal{O}(t^\alpha)$' means 'up to and including $\mathcal{O}(t^\alpha)$'.

In fact in this paper we shall show that under quite general conditions, the main one being that the velocities of the particles are Gaussian ('normal') distributed and independent of each other and of their positions, one can prove the following:

Theorem. Consider a classical mechanical system of N degrees of freedom ('particles'), described by positions r_i and velocities v_i ($i = 1 \ldots N$), collectively denoted by r^N and v^N, respectively, and whose time evolution is given by the equations of motion

$$\begin{aligned} \dot{r}_i &= v_i && (3) \\ m_i \dot{v}_i &= F_i(r^N, t) && (4) \end{aligned}$$

with arbitrary masses m_i and velocity-independent and smooth forces F_i. If the initial ensemble is described by a probability distribution in which each velocity is Gaussian and independent of the other velocities and the positions of all the particles, *i.e.*, it is of the form

$$P(r^N, v^N) = f(r^N) \prod_{i=1}^{N} \frac{\exp\left[-\frac{1}{2}\beta_i m_i (v_i - u_i)^2\right]}{\sqrt{2\pi/(m_i\beta_i)}}. \tag{5}$$

then the cumulants κ_n (defined below) of the displacements

$$\Delta r_i(t) \equiv r_i(t) - r_i(0) \tag{6}$$

obey

$$\kappa_n = \begin{cases} c_n t^n + \mathcal{O}(t^{n+1}) & \text{for } n \leq 2 \\ c_n t^{2n} + \mathcal{O}(t^{2n+1}) & \text{for } n > 2 \end{cases} \tag{7}$$

for sufficiently short initial times t (and where the coefficients c_n will be given later in Eq. (36)).

We stress that in this Theorem the forces are independent of the velocities, but may depend on the positions r^N and on the time t in any way as long as they are smooth. An example of smooth forces would be infinitely differentiable forces $F_i(r^N, t)$, but also Lennard-Jones forces are allowed provided the distribution of the the positions $f(r^N)$ assigns a vanishing probability for the particles to be at zero distance of one another, which is the singular point of the Lennard-Jones potential at which it is not smooth.

Furthermore, we note that the initial distribution in Eq. (5) is not an equilibrium distribution, but valid for a system consisting of particles with different individual masses m_i, mean velocities u_i and "temperatures" β_i. Furthermore, there is no restriction to the distribution of positions $f(r^N)$.

The distribution in Eq. (5) shares, however, with the equilibrium distribution its Gaussian dependence on the velocities, which is crucial for the Theorem to hold.

Canonical equilibrium for a single or multi-component fluid is just a special case of the systems covered by the Theorem. In that case, one has $F_i = -\partial U/\partial r_i$, $f(r^N) \propto \exp[-\beta U(r^N)]$, $u_i = 0$ and $\beta_i = \beta$.

The probability distribution functions of the form in Eq. (5), in which each particle has its own mean velocity u_i and 'temperature' β_i, may seem of a mathematical generality which has little physical relevance. Note however that this is a convenient way to describe mixtures of any arbitrary number of components. In such a mixture, the mean velocities and temperatures of the different components could be selected physically *e.g.* by means of a laser (or perhaps even a neutron beam), tuned to a resonance of one of the components only, which would give the particles of that component a nonzero average momentum as well as a different initial 'temperature' β_i due to the recoil energy.[10]

The proof we will present below is a "physicists' proof", meaning that the proof does not claim to have complete mathematical rigor but has every appearance of being correct, perhaps under mild and reasonable additional conditions such as a finite radius of convergence of various series as well as the existence of the moments and cumulants.

The paper is structured as follows. In section 2, we give some definitions to be able to treat the cumulants in more detail. In section 3, we give the steps needed to prove the main Theorem. In it, we need an auxiliary theorem concerning general Gaussian distributed variables whose proof is postponed to the Appendix. The coefficients c_n in Eq. (7) of the Theorem are determined in section 3 as well. We conclude with a discussion of the results and their broader physical relevance in section 4.

2 Moments and cumulants

In this paper, when we speak of a 'variable' we mean a function of the positions r^N and the velocities v^N and possibly the time t. All physical quantities are variables of this kind. For such variables $X(r^N, v^N, t)$, the average with respect to the distribution function $P(r^N, v^N)$ will be denoted by

$$\langle X \rangle = \int dr^N dv^N \, P(r^N, v^N) X(r^N, v^N, t). \tag{8}$$

The displacement of each degree of freedom or particle i in time t was defined in Eq. (6). Note that $\Delta r_i(t)$ is the displacement of *one* particle i, so throughout, i will stay fixed, although it may have any value between

1 and N. Its nth moment[2] is the average of the nth power of the displacement, *i.e.*,

$$\mu_n \equiv \langle \Delta r_i^n(t) \rangle, \tag{9}$$

where the dependence on i and t on the left hand side (lhs) was suppressed. The cumulants of $\Delta r_i(t)$,[2] denoted by κ_n, are equal to these moments with certain factorizations of them subtracted and thus sensitive to the correlations of $\Delta r_i(t)$. Their precise definition is via the cumulant generating function[23, 24]

$$\Phi(k) \equiv \log \langle \exp[\mathrm{i}k\Delta r_i(t)] \rangle = \sum_{n=1}^{\infty} \frac{\kappa_n}{n!}(\mathrm{i}k)^n. \tag{10}$$

from which the κ_n follow as

$$\kappa_n \equiv \left. \frac{\partial^n \Phi}{\partial(\mathrm{i}k)^n} \right|_{k=0}. \tag{11}$$

An alternative notation for the cumulants, which is more analogous to Eq. (9) and which is especially convenient in the case of several variables, is[24]

$$\langle\!\langle \Delta r_i^n(t) \rangle\!\rangle \equiv \kappa_n. \tag{12}$$

The cumulant generating function in Eq. (10) can be expressed in terms of the moments μ_n since $\Phi(k) = \log\langle \exp[\mathrm{i}k\Delta r_i(t)]\rangle = \log[1+\sum_{n=1}^{\infty}(\mathrm{i}k)^n \mu_n/n!]$. The relations between the cumulants and moments can then be found by Taylor expanding the logarithm around 1 and using a multinomial expansion for the resulting power series. This gives, somewhat formally,

$$\kappa_n \;=\; -n! \sum_{\substack{p_\ell \geq 0 \\ \sum_{\ell=1}^{\infty} \ell p_\ell = n}} \Big(\sum_{\ell=1}^{\infty} p_\ell - 1 \Big)! \prod_{\ell=1}^{\infty} \frac{\big(-\mu_\ell/\ell!\big)^{p_\ell}}{p_\ell!} \tag{13}$$

For instance, for the first few κ_n, Eq. (13) becomes $\kappa_1 = \mu_1$, $\kappa_2 = \mu_2 - \mu_1^2$ and $\kappa_3 = \mu_3 - 3\mu_1\mu_2 + 2\mu_1^3$.[23, 24, 26] In general, $\kappa_n = \mu_n \pm$ factored terms, where the factored terms contain all ways of partitioning the moment μ_n into a product of lower moments μ_ℓ such that all ℓ values (taking into account the 'frequencies of occurrence' p_ℓ) add up to n.

Apart from the cumulants κ_n of the single variable $\Delta r_i(t)$, we will also need the general definition of cumulants which applies to any number of

[2] Although the moments μ_n and cumulants κ_n are really the 'moments and cumulants of the probability distribution function of $\Delta r_i(t)$,' we will refer to them simply as the 'moments and cumulants of $\Delta r_i(t)$.'

variables. These are defined as follows.[23, 24] For a set of variables X_γ ($\gamma = 1 \dots \alpha$) the cumulant generating function is defined as

$$\Phi(k_1, \dots k_\alpha) \equiv \log \Big\langle \exp \sum_{\gamma=1}^{\alpha} \mathrm{i} k_\gamma X_\gamma \Big\rangle. \tag{14}$$

With the help of this generating function, the cumulants can be expressed similarly as in Eq. (11) by

$$\langle\!\langle X_1^{n_1} \dots X_\alpha^{n_\alpha} \rangle\!\rangle \equiv \left(\prod_{\gamma=1}^{\alpha} \frac{\partial^{n_\gamma}}{\partial(\mathrm{i}k_\gamma)^{n_\gamma}} \right) \Phi(k_1, \dots k_\alpha) \Bigg|_{k_{1\dots\alpha}=0}. \tag{15}$$

(Note that $k_{1\dots\alpha} = k$ is a short-hand notation for $k_1 = k$, $k_2 = k$, $\dots$, $k_\alpha = k$.) The cumulants can be expressed in terms of moments analogously to Eq. (13):

$$\begin{aligned} &\langle\!\langle X_1^{n_1} \dots X_\alpha^{n_\alpha} \rangle\!\rangle \\ &= -n_1! \cdots n_\alpha! \sum_{\substack{p_{\{\ell\}} \geq 0 \\ \sum_{\{\ell\}} \ell_\gamma p_{\{\ell\}} = n_\gamma}} \Big(\sum_{\{\ell\}} p_{\{\ell\}} - 1 \Big)! \prod_{\{\ell\}} \frac{1}{p_{\{\ell\}}!} \left(- \frac{\langle X_1^{\ell_1} \dots X_\alpha^{\ell_\alpha} \rangle}{\ell_1! \cdots \ell_\alpha!} \right)^{p_{\{\ell\}}}, \end{aligned} \tag{16}$$

where $\{\ell\} = \{\ell_1, \dots, \ell_\alpha\}$ denotes a set of nonnegative ℓ_γ values, $\gamma = 1 \dots \alpha$ and $p_{\{\ell\}}$ gives the frequency of occurrence of that set. In Eq. (16) the sum is over the frequencies of all possible sets $\{\ell\}$ (and thus all possible moments $\langle X_1^{\ell_1} \dots X_\alpha^{\ell_\alpha} \rangle$) for which $\sum_{\ell=1}^{\infty} \ell_\gamma p_{\{\ell\}} = n_\gamma$. This is nothing else but factorizing the expression $X_1^{n_1} \dots X_\alpha^{n_\alpha}$ in all possible ways. Hence, the cumulants $\langle\!\langle X_1^{n_1} \dots X_\alpha^{n_\alpha} \rangle\!\rangle = \langle X_1^{n_1} \dots X_\alpha^{n_\alpha} \rangle \pm$ factored terms that are products of the moments $\langle X_1^{\ell_1} \dots X_\alpha^{\ell_\alpha} \rangle$ such that the ℓ_γ values for fixed γ add up (taking into account their frequencies $p_{\{\ell\}}$) to n_γ.

3 Proof of the main Theorem

Strategy based on Gaussian velocities

The Theorem formulated in Eqs. (3–7) in section 1 will be proved in this section, although we will defer the details of the proof of a required auxiliary theorem to the Appendix for greater clarity.

To obtain the initial, short time behavior of the moments and cumulants of the displacement, $\Delta r_i(t)$ may be Taylor-MacLaurin expanded around $t = 0$ as

$$\Delta r_i(t) = \sum_{\gamma=1}^{\infty} \frac{t^\gamma}{\gamma!} \frac{d^\gamma r_i}{dt^\gamma}\Big|_{t=0} = \sum_{\gamma=1}^{\infty} \frac{t^\gamma}{\gamma!} \frac{d^{\gamma-1} v_i}{dt^{\gamma-1}}\Big|_{t=0} \tag{17}$$

where we used (3). Because of the equations of motion (3) and (4), the $d^\gamma v_i/dt^\gamma$, viewed as functions of r^N, v^N and t, are recursively related by

$$\frac{d^{\gamma+1}v_i}{dt^{\gamma+1}} = \sum_{j=1}^{N}\left[\frac{\partial}{\partial r_j}\Big(\frac{d^\gamma v_i}{dt^\gamma}\Big)v_j + \frac{\partial}{\partial v_j}\Big(\frac{d^\gamma v_i}{dt^\gamma}\Big)\frac{F_j}{m_j}\right] + \frac{\partial}{\partial t}\Big(\frac{d^\gamma v_i}{dt^\gamma}\Big). \tag{18}$$

To show that $\kappa_n = \mathcal{O}(t^{2n})$, it is of course possible to straightforwardly work out κ_n, using Eqs. (13), (9), (17), (18), (8) and (5), in that order. Such a procedure was essentially followed by Schofield[2] for $n \le 6$ and Sears[7] for $n \le 8$ for equilibrium fluids. In their expressions many cancellations occurred before κ_n could be seen to be, for these cases, of the $2n$-th order in t instead of the n-th order in t. These cancellations seemed to happen as a consequence of equilibrium properties. However, by carrying out the same straightforward procedure for the more general class of non-equilibrium initial conditions in Eq. (5), we have found that while odd moments are no longer zero still $\kappa_n = \mathcal{O}(t^{2n})$ for $n = 3$, 4, 5 and 6. These results for κ_3, κ_4, κ_5 and κ_6 naturally led us to propose the Theorem. Because the straightforward calculations for κ_3, κ_4, κ_5, and κ_6 for this non-equilibrium case are very lengthy, they will not be presented here. In any case this procedure is not very suited to determine the order in t of κ_n for general n, because with increasing n an increasing number of terms have to be combined (taking together equal powers of t from the various products of moments) before they can be shown to be zero.

Our strategy for proving that the nth cumulant $\langle\langle\Delta r_i^n\rangle\rangle = \mathcal{O}(t^{2n})$ for all $n > 2$, will be to exploit the Gaussian distribution of the velocities as much as possible. But we can only hope to use the Gaussian nature of the velocities if we succeed in bringing out explicitly the dependence of the coefficients of the power series in t of the cumulants of the velocities. This dependence has so far only been given implicitly — the cumulants are related to the moments by Eq. (13), the moments contain $[\Delta r_i]^\ell$, Δr_i is expanded in the time t in Eq. (17), and the coefficients in that expansion are the derivatives of the velocity v_i whose dependence on the positions, the velocities and the time can be found by using Eq. (18) recursively. To make this more explicit, the first part of the proof will be to expand the cumulants as a powers series in the time t and the second part will be to express this series more explicitly in the velocities. In the third and last part we will then use the properties of Gaussian distributed variables, *i.e.*, the velocities, to complete the proof of the main Theorem.

It turns out that the properties of Gaussian distributed variables that we will require in the third part of the proof are formulated for Gaussian variables whose mean is zero, while in Eq. (5) the velocities are Gaussian but do not have zero mean. For this reason, it is convenient to introduce already at this point new velocity variables whose mean is zero (cf. Eq. (5)):

$$V_i \equiv v_i - \langle v_i \rangle = v_i - u_i. \tag{19}$$

The V_i are generalizations of the peculiar velocities used in local equilibrium situations and will be referred to in the general case treated in this paper as *peculiar velocities* as well. Substituting Eq. (19) into the probability distribution Eq. (5) and the time expansion in (17), gives them in their peculiar velocity form:

$$P(r^N, V^N) \;=\; f(r^N) \prod_{i=1}^{N} \frac{\exp\left[-\frac{1}{2}\beta_i m_i V_i^2\right]}{\sqrt{2\pi/(m_i\beta_i)}} \tag{20}$$

$$\Delta r_i(t) \;=\; u_i t + \sum_{\gamma=1}^{\infty} \frac{t^\gamma}{\gamma!} \frac{d^{\gamma-1}V_i}{dt^{\gamma-1}}. \tag{21}$$

In order to make future expressions less complicated we introduce for the coefficients in Eq. (21) the notation ($\gamma = 1,\, 2,\, \ldots$)

$$X_\gamma = \frac{1}{\gamma!} \frac{d^{\gamma-1}V_i}{dt^{\gamma-1}}. \tag{22}$$

Thus *e.g.* $X_1 = V_i$ and Eq. (21) becomes

$$\Delta r_i(t) = u_i t + \sum_{\gamma=1}^{\infty} X_\gamma t^\gamma, \tag{23}$$

The recursion relation between the coefficients X_γ is, from Eqs. (18) and (22):

$$\frac{X_{\gamma+1}}{\gamma+1} \;=\; \sum_{j=1}^{N} \left[\frac{\partial X_\gamma}{\partial r_j}(u_j + V_j) + \frac{\partial X_\gamma}{\partial V_j} \frac{F_j}{m_j} \right] + \frac{\partial X_\gamma}{\partial t}. \tag{24}$$

We will now start the actual proof of the Theorem for general n.

First part: Expanding the cumulants in the time t

The infinite number of terms in the time expansion Δr_i in Eq. (23) means that we would have to combine in Eq. (13) an infinite number of terms to get the power expansion in t of the cumulants. Obviously if we are interested in the cumulants up to $\mathcal{O}(t^{2n-1})$ we should not have to retain all these terms in Eq. (23), but only those up to $\mathcal{O}(t^{2n-1})$. As a matter of fact, we need even less terms, namely only terms up to $\mathcal{O}(t^n)$ in Eq. (23), as the following reasoning shows. The moments μ_ℓ which occur in the expression in Eq. (13)

for the cumulants κ_n, can be worked out by taking the terms up to the n-th order in t in Eq. (23), which gives

$$\mu_\ell = \Big\langle \big[u_i t + X_1 t + \ldots + X_n t^n\big]^\ell + \mathcal{O}(t^{\ell+n}) \Big\rangle . \tag{25}$$

A product of two μ_ℓ's can then be written as

$$\begin{aligned}\mu_{\ell_1}\mu_{\ell_2} &= \Big\langle \big[u_i t + X_1 t + \ldots + X_n t^n\big]^{\ell_1} \Big\rangle \Big\langle \big[u_i t + X_1 t + \ldots + X_n t^n\big]^{\ell_2} \Big\rangle \\ &\quad + \mathcal{O}(t^{\ell_1+\ell_2+n}). \end{aligned}\tag{26}$$

Applying this recursively to a product of μ_{ℓ_γ} ($\gamma = 1\ldots\alpha$), the remainder term in replacing the full expression for $\Delta r_i(t)$ by the first n terms is $\mathcal{O}(t^{\sum_{\gamma=1}^{\alpha}\ell_\gamma+n})$. If some of the ℓ_γ values occur more than once in this product, this can be rewritten as $\mathcal{O}(t^{\sum_{\ell=1}^{\infty}\ell p_\ell+n})$, where p_ℓ is the frequency of occurrence of ℓ. According to Eq. (13), the nth cumulant is a sum of terms which are products of μ_ℓ with frequencies p_ℓ such that the ℓp_ℓ add up to n, *i.e.* $\sum_\ell \ell p_\ell = n$, so for each of those terms the remainder in replacing the full expression for $\Delta r_i(t)$ by the first n terms, is $\mathcal{O}(t^{2n})$ and

$$\kappa_n = \Big\langle\!\Big\langle \Big[u_i t + \sum_{\gamma=1}^{n} X_\gamma t^\gamma\Big]^n \Big\rangle\!\Big\rangle + \mathcal{O}(t^{2n}). \tag{27}$$

We remark that the first term on the right hand side (rhs) of this equation gives all powers t^n up to t^{2n-1}, which we are interested in, as well as some of the higher powers of $t^{\alpha\geq 2n}$ which we are not interested in. The second term, *i.e.*, $\mathcal{O}(t^{2n})$ only contains higher powers of $t^{\alpha\geq 2n}$. So with Eq. (27) we have established that for the lower powers only n terms in the time expansion of $\Delta r_i(t)$ are needed, but we have not separated the powers of t lower and higher than $2n$ completely yet.

For that purpose we continue from Eq. (27) and use first the translation invariance property of cumulants, which states that $\langle\!\langle (X+C)^n\rangle\!\rangle = \langle\!\langle X^n\rangle\!\rangle$ if $n>1$ and C a constant while for $n=1$ one has $\langle\!\langle X+C\rangle\!\rangle = \langle\!\langle X\rangle\!\rangle + C$,[23, 24] to obtain from Eq. (27) (with $C = u_i t$)

$$\kappa_n = \Big\langle\!\Big\langle \Big[\sum_{\gamma=1}^{n} X_\gamma t^\gamma\Big]^n \Big\rangle\!\Big\rangle + u_i t\,\delta_{n1} + \mathcal{O}(t^{2n}). \tag{28}$$

Furthermore, we can write the first term on the rhs of in this expression, using Eqs. (14) and (15) with $\alpha = 1$ and $k_1 = k$, as

$$\begin{aligned}\Big\langle\!\Big\langle \Big[\sum_{\gamma=1}^{n} X_\gamma t^\gamma\Big]^n \Big\rangle\!\Big\rangle &= \frac{\partial^n}{\partial(\mathrm{i}k)^n}\log\Big\langle \exp\sum_{\gamma=1}^{n}\mathrm{i}kX_\gamma t^\gamma\Big\rangle\Big|_{k=0} \\ &= \frac{\partial^n}{\partial(\mathrm{i}k)^n}\left[\log\Big\langle \exp\sum_{\gamma=1}^{n}\mathrm{i}k_\gamma X_\gamma t^\gamma\Big\rangle\Big|_{k_{1\ldots n}=k}\right]\Bigg|_{k=0}. \end{aligned}\tag{29}$$

The introduction of the k_γ ($\gamma = 1 \ldots n$) here may seem unnecessary, as they are all set equal to k and subsequently to zero at the end, but now one can use the chain rule and a multinomial expansion to find from Eq. (29)

$$\begin{aligned}\left\langle\!\!\left\langle \Big[\sum_{\gamma=1}^{n} X_\gamma t^\gamma\Big]^n \right\rangle\!\!\right\rangle &= \left(\sum_{\gamma=1}^{n} \frac{\partial}{\partial(\mathrm{i}k_\gamma)}\right)^n \log\left\langle \exp\sum_{\gamma=1}^{n} \mathrm{i}k_\gamma X_\gamma t^\gamma\right\rangle\Big|_{k_{1\ldots n}=0} \\ &= \sum_{\substack{n_\gamma\geq 0\\ \sum_{\gamma=1}^n n_\gamma = n}} \frac{n!}{n_1!\cdots n_n!} \\ &\qquad \times \prod_{\gamma=1}^{n} \frac{\partial^{n_\gamma}}{\partial(\mathrm{i}k_\gamma)^{n_\gamma}} \log\left\langle \exp\sum_{\gamma=1}^{n} \mathrm{i}k_\gamma X_\gamma t^\gamma\right\rangle\Big|_{k_{1\ldots n}=0}, \end{aligned} \tag{30}$$

where on the rhs of Eq. (30) we now recognize the multi-variable cumulant defined in Eqs. (14) and (15) with $\alpha = n$, whence

$$\left\langle\!\!\left\langle \Big[\sum_{\gamma=1}^{n} X_\gamma t^\gamma\Big]^n \right\rangle\!\!\right\rangle = \sum_{\substack{n_\gamma\geq 0\\ \sum_{\gamma=1}^n n_\gamma = n}} \frac{n!}{n_1!\cdots n_n!} \langle\!\langle X_1^{n_1} X_2^{n_2} \ldots X_n^{n_n}\rangle\!\rangle t^{\sum_{\gamma=1}^n n_\gamma \gamma}. \tag{31}$$

For κ_n in Eq. (28), we need this quantity only explicitly up to $\mathcal{O}(t^{2n-1})$, so powers of t higher than $2n-1$ may be discarded (*i.e.*, combined with the $\mathcal{O}(t^{2n})$ term) and only powers $t^{\alpha<2n}$ need to be kept. Hence, in the exponent on the rhs of Eq. (31), we only need terms with $\sum_{\gamma=1}^n n_\gamma\gamma < 2n$. Since also $n = \sum_{\gamma=1}^n n_\gamma$, we obtain $\sum_{\gamma=1}^n n_\gamma\gamma < 2\sum_{\gamma=1}^n n_\gamma$, or $n_1 > \sum_{\gamma=2}^n n_\gamma(\gamma-2)$. Combining this condition with Eqs. (28) and (31), and using $X_1 = V_i$ (cf. Eq. (22)), we find that the expansion of κ_n in time t up to $\mathcal{O}(t^{2n-1})$ is given by

$$\kappa_n = \sum_{\substack{n_\gamma\geq 0\\ \sum_{\gamma=1}^n n_\gamma = n\\ n_1 > \sum_{\gamma=2}^n n_\gamma(\gamma-2)}} \frac{n!}{n_1!\cdots n_n!} \langle\!\langle V_i^{n_1} X_2^{n_2} \ldots X_n^{n_n}\rangle\!\rangle t^{\sum_{\gamma=1}^n n_\gamma \gamma} + u_i t\,\delta_{n1} + \mathcal{O}(t^{2n}). \tag{32}$$

We note that in Eq. (32) only cumulants appear, instead of moments, and, more importantly, that each power of t is easily identified and we have separated the powers of t lower and higher than $2n$, something that in the straightforward moment-based approach mentioned above only happens after a lengthy calculation.

Second part: Writing cumulants in terms of velocities

The dependence of κ_n in Eq. (32) on the peculiar velocities V^N follows from the dependence of the X_γ on the V^N. We note that for $\gamma \geq 2$, X_γ is a polynomial in the peculiar velocities V^N of degree $\gamma - 2$, with coefficients that can depend on the positions of the particles and the time, as can be seen inductively as follows. For $\gamma = 2$, Eqs. (22), (19) and (4) show that $X_2 = (dV_i/dt)/2 = F_i(r^N, t)/(2m_i)$, which is independent of V^N so it is a polynomial in the peculiar velocities of degree zero. Using the recursion relation Eq. (24) one now sees that if X_γ is a polynomial in V^N of degree $\gamma-2$ then on the rhs of Eq. (24), the term $(u_j + V_j)\partial X_\gamma/\partial r_j$ is a polynomial of degree $\gamma - 1$, while $(F_j/m_j)\partial X_\gamma/\partial V_j$ has a degree of $\gamma - 3$, and $\partial X_\gamma/\partial t$ has a degree $\gamma - 2$. The highest power of V^N in $X_{\gamma+1}$ is thus indeed $\gamma - 1$.

Therefore we can write for the dependence of X_γ on V^N

$$X_\gamma = \sum_{p=0}^{\gamma-2} \sum_{\sum_j p_j = p} a_{\{p_j\}}(r^N, t) V_1^{p_1} \cdots V_N^{p_N} \tag{33}$$

or, focusing on powers of V_i,

$$X_\gamma = \sum_{p_i=0}^{\gamma-2} b_{\{p_j\}}(r^N, V_{j\neq i}^N, t)\, V_i^{p_i} \tag{34}$$

As it turns out, in the third part of the proof we will only need this polynomial nature, while the precise and explicit forms of $a_{\{p_j\}}(r^N, t)$ or $b_{\{p_j\}}(r^N, V_{j\neq i}^N, t)$ are not required.

Third part: Using the Gaussian nature of velocities

Given the polynomial nature of the X_γ as a function of V_i in Eq. (34), we see that in the second condition under the summation sign in Eq. (32), *i.e.*, $n_1 > \sum_{\gamma=2}^n n_\gamma(\gamma-2)$, the expression $n_\gamma(\gamma-2)$ is also the degree in V_i of the polynomial $X_\gamma^{n_\gamma}$ which occurs on the rhs of Eq. (34). Then, $\sum_{\gamma=2}^n n_\gamma(\gamma-2)$, which we will denote by d, is also the combined degree of the product of $X_2^{n_2}$ up to $X_n^{n_n}$ that occurs in Eq. (32). Thus the sum in Eq. (32) is over cumulants for which the power n_1 of the peculiar velocity V_i is higher than the combined degree d of $X_2^{n_2} \cdots X_n^{n_n}$.

The auxiliary Theorem A in the Appendix can then be applied to cumulants of this form $\langle\!\langle V_i^{n_1} X_2^{n_2} \ldots X_n^{n_n} \rangle\!\rangle$. Theorem A states that if X_γ ($\gamma = 2 \ldots n$) are polynomials of degree d_γ in a zero-mean Gaussian distributed V, and n_γ are nonnegative integers, then $\langle\!\langle V^{n_1} X_2^{n_2} \ldots X_n^{n_n} \rangle\!\rangle = 0$ if $n_1 > d \equiv \sum_{\gamma=2}^n n_\gamma d_\gamma$, except when all $n_{\gamma\geq 2} = 0$ and $n_1 = 2$, in which case $\langle\!\langle V^{n_1} X_2^{n_2} \ldots X_n^{n_n} \rangle\!\rangle = \langle\!\langle V^2 \rangle\!\rangle$.

We can therefore complete the proof of the main Theorem by applying the auxiliary Theorem A to each term in the summation on the rhs of Eq. (32), with $V = V_i$ and $d_\gamma = \gamma - 2$ (see Eq. (34)). Note that the variables $V_{j\neq i}$ and r_i are independent of V_i, so that even though Theorem A is only formulated for the average of $V = V_i$, we may afterwards also average over the other degrees of freedom and still get the properties of Theorem A.

The degree d mentioned in Theorem A is for our case given by $d = \sum_{\gamma=2}^{n} n_\gamma d_\gamma = \sum_{\gamma=2}^{n} n_\gamma(\gamma - 2)$. As the restriction on the summation in Eq. (32) shows, for each explicit term in the sum in Eq. (32), n_1 is larger than this d. Then Theorem A tells us that the cumulant occurring in each term is zero except when $n_2 = n_3 = \cdots n_n = 0$ and $n_1 = 2$. This exception means, since also $\sum_{\gamma=1}^{n} n_\gamma = n$, that $n = n_1 = 2$. So the only possible nonzero term in the sum in Eq. (32) occurs for $n = 2$. Furthermore, for $n = 1$, only the last term $u_i t\, \delta_{n1}$ in Eq. (32) is left.

Thus, using Theorem A, we have shown that each term in Eq. (32) is zero separately except for $n = 1$ and $n = 2$, so that

$$\kappa_n = \begin{cases} \mathcal{O}(t^{2n}) & \text{if } n > 2 \\ \mathcal{O}(t^{n}) & \text{if } n \leq 2 \end{cases} \tag{35}$$

remains on the rhs of Eq. (32). Given that κ_n was expanded here as a power series in t, Eq. (35) coincides with the formulation Eq. (7) of the main Theorem, which is therefore now proved (with the proviso that Theorem A is proved in the Appendix). □

An expression for the coefficient c_n in the Theorem

We will now determine the coefficient of t^{2n} in κ_n, *i.e.*, the c_n of Eq. (7) of the Theorem. For $n = 1$ and $n = 2$ it is straightforward to show that

$$c_1 = \langle v_i \rangle = u_i \tag{36a}$$

$$c_2 = \langle V_i \rangle = 1/(\beta_i m_i). \tag{36b}$$

To find c_n for $n > 2$ one can use the same calculation of κ_n as used above, but one has to take one additional term $X_{n+1}t^{n+1}$ in the time expansion of $\Delta r_i(t)$ in Eq. (27), *i.e.*, one writes $\kappa_n = \langle\!\langle [u_i t + \sum_{\gamma=1}^{n+1} X_\gamma t^\gamma]^n \rangle\!\rangle + \mathcal{O}(t^{2n+1})$. Performing then the same kind of manipulations as in the proof above one arrives at

$$c_{n>2} = \sum_{\substack{n_\gamma \geq 0 \\ \sum_{\gamma=1}^{n+1} n_\gamma = n \\ \sum_{\gamma=1}^{n+1} \gamma n_\gamma = 2n}} \frac{n!}{n_1! \cdots n_{n+1}!} \langle\!\langle V_i^{n_1} X_2^{n_2} \ldots X_{n+1}^{n_{n+1}} \rangle\!\rangle. \tag{36c}$$

Examples of this for $n = 3$ and $n = 4$ are

$$c_3 = 3\langle\!\langle V_i^2 X_4 \rangle\!\rangle + 6\langle\!\langle V_i X_2 X_3 \rangle\!\rangle + \langle\!\langle X_2^3 \rangle\!\rangle \tag{37}$$

$$\begin{aligned} c_4 = {} & 4\langle\!\langle V_i^2 X_5 \rangle\!\rangle + 6\langle\!\langle V_i^2 X_3^2 \rangle\!\rangle + 12\langle\!\langle V_i^2 X_2 X_4 \rangle\!\rangle \\ & +12\langle\!\langle V_i X_2^2 X_3 \rangle\!\rangle + \langle\!\langle V_2^4 \rangle\!\rangle. \end{aligned} \tag{38}$$

Although the X_γ are useful to derive these expressions for c_n, to evaluate the c_n in practice requires additional work. One would first need to write the X_γ out as $d^{\gamma-1}V_i/t^{\gamma-1}$ (cf. Eq. (22)) and work out the derivatives of V_i using the recursion relation (18). Furthermore, the cumulants would have to be worked out in terms of averages. The values of these averages will depend on the system and their evaluation will in general require a numerical approach.

4 Applications and discussion

In this paper we have presented and proved a theorem that states that nth order cumulant of the displacement of a single particle scales as t^{2n} for small t and all $n > 2$ for a large class of systems for which the initial velocities are Gaussian and independent.

While it is true that only displacements in one direction are considered, for isotropic systems, the result may be translated to displacements in more than one dimension. Work on the solution for non-isotropic systems is underway.

We will now discuss a number of applications of the Theorem just proved.

1) The equilibrium Van Hove self-correlation function. a) In incoherent neutron scattering on an equilibrium fluid, one essentially measures the equilibrium Van Hove self-correlation function $G_s(r,t)$, which is the Fourier inverse of the incoherent scattering function $F_s(k,t)$.[1, 8–12] If the wave vector k in $F_s(k,t)$ is small, then according to Eq. (2) $F_s(k,t) \approx \exp[-\kappa_2 k^2/2]$, *i.e.*, nearly Gaussian, and so its inverse Fourier transform $G_s(r,t)$ is also approximately Gaussian. Corrections to this Gaussian behavior can be found by resumming $F_s(k,t) = \exp\sum_n \kappa_n (\mathrm{i}k)^n/n!$ in Eq. (2) to the form

$$F_s(k,t) = e^{-\frac{1}{2}\kappa_2 k^2}\left[1+\sum_{n=2}^{\infty}(-1)^n b_{2n}k^{2n}\right] \tag{39}$$

using that odd cumulants are zero. The coefficients b_{2n} are given by

$$b_{2n} = \sum_{\substack{p_\ell\geq 0\\ \sum_{\ell=2}^{\infty}\ell p_\ell = n}} \prod_{\ell=2}^{\infty}\left[\frac{1}{p_\ell!}\left(\frac{\kappa_{2\ell}}{(2\ell)!}\right)^{p_\ell}\right]. \tag{40}$$

Fourier inverting the resummed form of $F_s(k,t)$ leads to

$$G_s(r,t) = \frac{e^{-w^2}}{\sqrt{2\pi\kappa_2}}\left[1+\sum_{n=2}^{\infty}\frac{b_{2n}}{(2\kappa_2)^n}H_{2n}(w)\right], \tag{41}$$

where H_n is the nth Hermite polynomial and the dimensionless $w \equiv r/\sqrt{2\kappa_2}$. We note that the series in Eq. (41) appears to have a fairly rapid convergence.[6] Taking just the first few terms would give

$$G_s(r,t) = \frac{e^{-w^2}}{\sqrt{2\pi\kappa_2}}\left[1 + \frac{\kappa_4}{4!4\kappa_2^2}H_4(w) + \frac{\kappa_6}{6!8\kappa_2^3}H_6(w) + \dots\right]. \tag{42}$$

The current Theorem provides a justification for the expansion in Eq. (41) of the self part of the Van Hove function G_s for short times t. As Eqs. (40) and (41) show, the cumulants $\kappa_{n\geq 4}$ give, via the b_{2n}, corrections to a Gaussian behavior of $G_s(r,t)$. The Gaussian factor e^{-w^2} suggests that typical values of w are $\mathcal{O}(1)$ in Eq. (41), so also $H_{2n}(w) = \mathcal{O}(1)$. Its prefactor in Eq. (41) is, however, t-dependent through $b_{2n}/(2\kappa_2)^n$. Given the relation between b_n and κ_n in Eq. (40) it is easy to see that they scale similarly, *i.e.*, if the conditions of the Theorem are satisfied so that $\kappa_{n>2} = \mathcal{O}(t^{2n})$ then also $b_n = \mathcal{O}(t^{2n})$. Since $\kappa_2 = \mathcal{O}(t^2)$, we obtain

$$\frac{b_{2n}}{(2\kappa_2)^n} = \mathcal{O}(t^{2n}). \tag{43}$$

This means that the series in Eq. (41) *is well-behaved for small times* t*, in that each next term is smaller than the previous one, and that by truncating the series one obtains for small* t *approximations which can be systematically improved by taking more terms into account. Note that in contrast if* κ_n *had been* $\mathcal{O}(t^n)$*, each term in the series in Eq.* (51) *would have been of the same order.*

b) An expansion of a similar form as Eq. (41) was found by Rahman[4] for $G_s(r,t)$, and by Nijboer and Rahman[5] for $F_s(k,t)$. Their expressions are in terms of the so-called *non-Gaussian parameters* α_n. These non-Gaussian parameters have recently also found an application in the context of supercooled liquids and glasses, where they have been proposed as a kind of order parameter for the glass transition[11, 12, 18] and as measures of 'dynamical heterogeneities' in supercooled liquids and glasses.[19–22]

Given the interest in these non-Gaussian parameters α_n, we will now compare the cumulants κ_n with the α_n. The non-Gaussian parameters α_n are defined in terms of the distance $r = \sqrt{\Delta x_i^2(t) + \Delta y_i^2(t) + \Delta z_i^2(t)}$ traveled by a particle in time t in a three dimensional fluid, as[4]

$$\alpha_n \equiv \frac{\langle r^{2n}\rangle}{\langle r^2\rangle^n(2n+1)!!/3^n} - 1. \tag{44}$$

For isotropic fluids, $\langle r^{2n}\rangle = (2n{+}1)\,\langle\Delta x_i^{2n}(t)\rangle = (2n{+}1)\mu_{2n}$, so that Eq. (44) can be written as

$$\alpha_n = \frac{\mu_{2n} - (2n-1)!!\mu_2^n}{(2n-1)!!\mu_2^n}. \tag{45}$$

We now see that even though both the α_n and the cumulants $\kappa_{n>2}$ are, by construction, zero for Gaussian distributed variables, in Eq. (45) the α_n are $2n$-th moments μ_{2n} with only the most factored term, μ_2^n, subtracted, while the cumulants κ_{2n} in Eq. (13) have all possible factored terms subtracted. Using Eq. (45) and the inverse of the relation between κ_n and μ_n in Eq. (13), it is possible to express the α_n in terms of κ_n as

$$\alpha_n = n! \sum_{\substack{0\le p_\ell<n \\ \sum_{\ell=1}^\infty \ell p_\ell = n}} \prod_{\ell=1}^\infty \left[\frac{1}{p_\ell!}\left(\frac{2^\ell \kappa_{2\ell}}{(2\ell)!\kappa_2^\ell}\right)^{p_\ell}\right]. \tag{46}$$

According to this formal relation, the first few α_n are given by

$$\alpha_2 = \frac{1}{3}\frac{\kappa_4}{\kappa_2^2} \tag{47a}$$

$$\alpha_3 = \frac{\kappa_4}{\kappa_2^2} + \frac{1}{15}\frac{\kappa_6}{\kappa_2^3} \tag{47b}$$

The Theorem says that for small times t, $\kappa_2 = \mathcal{O}(t^2)$ and $\kappa_{n>2} = \mathcal{O}(t^{2n})$, so $\kappa_{2n}/\kappa_2^n = \mathcal{O}(t^{2n})$. According to Eq. (46), all α_n have a contribution from κ_4/κ_2^2, so that all α_n are of $\mathcal{O}(t^4)$, in contrast to the cumulants κ_{2n} which are of increasing order in t with increasing n. In fact, using Eq. (46) and the Theorem, one can derive straightforwardly that the dominant term for small t in Eq. (46) is the one with $p_1 = n-2$, $p_2 = 1$ and $p_{\ell>2} = 0$, which leads to

$$\alpha_n \sim \frac{n(n-1)}{2}\,\alpha_2 \tag{48}$$

plus a correction of $\mathcal{O}(t^6)$. Thus, for small t, α_3 is approximately three times α_2, α_4 six times α_2 *etc.* Such approximate relations are indeed borne out by Rahman's data on α_2, α_3 and α_4.[4, 8]

In terms of the α_n, the expansion of G_s in Eq. (42) becomes, with the help of Eq. (47),

$$G_s(r,t) = \frac{e^{-w^2}}{\sqrt{2\pi\kappa_2}}\left[1 + \frac{3\alpha_2}{4!4}H_4(w) + \frac{15(\alpha_3 - 3\alpha_2)}{6!8}H_6(w) + \dots\right]. \tag{49}$$

Although formally equivalent to Eq. (42), for small t Eq. (49) is somewhat less convenient, because one cannot see right away that the last term is $\mathcal{O}(t^6)$ rather than $\mathcal{O}(t^4)$, as one may naively suspect from $\alpha_2 = \mathcal{O}(t^4)$ and $\alpha_3 = \mathcal{O}(t^4)$. In Eq. (42), this time ordering is clear because the Theorem says that $\kappa_6 = \mathcal{O}(t^{12})$ and $\kappa_2 = \mathcal{O}(t^2)$.

We note that surprisingly, the data of Rahman also show that the relation between α_n and α_2 in Eq. (48) is still approximately satisfied for larger times.[4] This seems even true for hard spheres.[27] Thus the higher order

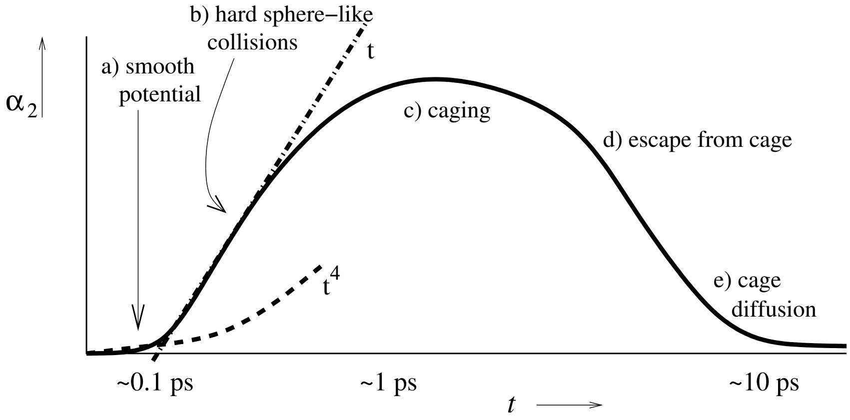

Figure 1: Sketch of the behavior of the non-Gaussian parameter $\alpha_2 = \kappa_4/(3\kappa_2^2)$ for regular liquids in equilibrium in different time regimes (based on fig. 7 in ref. [4] and fig. 4.11 in ref. [8]), with our physical interpretation for each regime.

non-Gaussian parameters $\alpha_{n>2}$ are apparently dominated by α_2 for larger times just as they are for smaller times t. This dominance of α_2 makes it hard to extract from these higher order non-Gaussian parameters any information that was not already contained in α_2. The cumulants κ_n, or perhaps the b_n, may contain additional information about correlations in (supercooled) fluids in a more accessible form (compared to the α_n), and may therefore be a more suitable choice to investigate such correlations for all times t.

c) Returning to the series in Eq. (41), although it may be well-behaved for small enough t, it is not known up to what time that remains so. Since $b_n = \mathcal{O}(t^{2n})$ only to leading order in t, the point at which the series in Eq. (41) is no longer guaranteed to be useful may be related to where the $\mathcal{O}(t^{2n})$ scaling of the κ_n breaks down. Rahman[4] (see also ref. [8] for a broader overview) investigated this and related questions numerically for a model of liquid argon (temperature 94 K, density $1.4 \cdot 10^3$ kg/m^3). Figure 1 shows a sketch of the non-Gaussian parameter α_2 as a function of t (based on fig. 7 in ref. [4] and fig. 4.11 in ref. [8]). One sees that α_2 is a very flat function near $t = 0$, which persists only up to roughly $t \approx 0.1$–0.2 ps. At that point the curve shoots up rapidly, giving a large 'hump' which last up to about 10 ps, and after which it starts to decrease to zero.

Although somewhat outside the scope of this paper, we would like to give an interpretation of the numerical results sketched in Figure 1. *a)* The flat behavior of α_2 near $t = 0$ is the $\mathcal{O}(t^4)$ behavior as given by the Theorem proved in this paper. *b)* Because hard spheres can be seen as a limit of a smooth interparticle potential in which the steepness goes to infinity,[7] and the potential used by Rahman is rather steep, the shoot-up phenomenon at ≈ 0.1 ps is probably related to the hard-spheres result of De Schepper *et al.*[25] that $\kappa_n = \mathcal{O}(|t|^{n+1})$, or $\alpha_2 = \mathcal{O}(|t|^5/t^4) = \mathcal{O}(|t|)$, as follows. The steep but smooth potential of Rahman will resemble a hard sphere fluid on time scales t_s on which a collision has been completed.[28] Thus at $t = t_s$ the scaling $\mathcal{O}(t^4)$ for α_2 ought to go over to $\mathcal{O}(|t|)$ which would require the kind of sharp increase observed by Rahman at ≈ 0.1 ps. *c)* The persistence of the non-Gaussianity occurs because the particle is trapped in a 'cage' formed by its neighboring particles, with which it has repeated and correlated collisions. *d)* The decay of α_2 to zero indicates that the motion becomes Gaussian and presumably sets in where the particle manages to escape its cage. After escaping it finds itself in a new cage environment consisting largely of particles with which it has not interacted before. This motion from cage to cage is called cage diffusion.[29] *e)* From a central limit theorem argument using that successively visited cages after many cage escapes have little correlation with each other, one would then expect Gaussian (and presumably but not necessarily diffusive) behavior.

Also in simulations of a supercooled argon-like mixture,[19] α_2 plotted as a function of time shows a flat curve for short times and a sharp increase around 0.1 ps, while $\alpha_3(t)$ shows similar behavior. The interesting part from the perspective of supercooled liquids and glasses, however, is in how far that increase continues and on what time scale and how α_2 decays back to zero, which takes a very long time for supercooled liquids and is related to the time scale at which the particle escapes its cage. But the Theorem has nothing to say about α_2 on that time scale.

2) Local equilibrium systems. In local equilibrium a fluid has roughly an equilibrium distribution except that the temperature, fluid velocity and density are spatially dependent. The class of initial distributions in Eq. (5) does not seem to be of that form, and indeed, if β_i and u_i are allowed to vary with r_i, then the proof as given here runs into difficulties. Nonetheless, one can construct distributions of the form (5) which physically describe precisely the local equilibrium situation. Imagine dividing the physical volume $\mathcal{V}$ up into A cells and assigning to each cell a a temperature β_a, a fluid velocity u_a and a density n_a. Divide the particles of the system up as well, putting $N_a = n_a\mathcal{V}/A$ particles in each cell, such that particles 1 through N_1 are in cell 1, $N_1 + 1$ through $N_1 + N_2$ are in cell 2 etc. This can be accomplished by choosing $f(r^N)$ in Eq. (5) such that the chance for these particles to be outside their cell is zero. Next, we set all the β_i and u_i of the particles in cell a to β_a and u_a. If the cells are big enough so that fluctuations in the number of particle may be neglected, this situation describes local equilibrium just as well as spatially dependent $\beta(r_i)$ and $u(r_i)$ can, and for this constructed local equilibrium, the Theorem holds.

3) Far-from-equilibrium phenomena on the picosecond time scale. The cumulants whose short time scaling was obtained here also occur naturally in the Green's function theory which was developed for far-from-equilibrium phenomena on the picosecond and nanometer scales.[13–17] Considering for example a mixture of two components, one can write the density of component λ ($\lambda = 1$ or 2) at position x and for simplicity in one dimension as:[17]

$$n_\lambda(x,t) = \int dx'\, G_\lambda(x,x',t) n_\lambda(x',0), \tag{50}$$

where the non-equilibrium *Green's function* $G_\lambda(x,x',t)$ is the probability that a particle of component λ is at position x at time t given that it was at position x' at time zero. By an expansion detailed in a future publication[17] G_λ can be written similarly as G_s in Eq. (41), as

$$G_\lambda(x,x',t) = \frac{e^{-w^2}}{\sqrt{2\pi\kappa_2}}. \left[1 + \sum_{n=3}^{\infty} \frac{b_n}{(2\kappa_2)^{n/2}} H_n(w)\right] \tag{51}$$

Here, the dimensionless $w \equiv (x - x' - \kappa_1)/\sqrt{2\kappa_2}$ and

$$b_n \;=\; \sum_{\substack{p_\ell \geq 0 \\ \sum_{\ell=3}^{\infty} \ell p_\ell = n}} \prod_{\ell=3}^{\infty} \left[\frac{1}{p_\ell !}\left(\frac{\kappa_\ell}{\ell !}\right)^{p_\ell}\right]. \tag{52}$$

Furthermore, in the Green's function theory, the κ_n, and thus the b_n through Eq. (52), depend on x' because in that theory the single particle i of component λ is required to have been at the position x' at time zero. This requirement can be imposed by multiplying the probability distribution function in Eq. (5) by $\delta(x_i - x')$ (times a proper normalization). The resulting distribution describes the subensemble of the original ensemble for which particle i is at x' at time zero. Note also that it is still of the same form as Eq. (5), with $f(r^N) \to f'(r^N) = \delta(x_i - x')f(r^N)$, so the Theorem still applies. Note that the $f(r^N)$ may describe any non-equilibrium distribution of the positions of the particles.

The Gaussian factor in Eq. (51) suggests as before that typical values of w are $\mathcal{O}(1)$, so $H_n(w) = \mathcal{O}(1)$. Its prefactor in Eq. (51) is $b_n/(2\kappa_2)^{n/2}$. Using the Theorem that $\kappa_n = \mathcal{O}(t^{2n})$ and the relation between b_n and κ_n in Eq. (52) it is easy to see that $b_n = \mathcal{O}(t^{2n})$. Since $\kappa_2 = \mathcal{O}(t^2)$, we obtain

$$\frac{b_n}{(2\kappa_2)^{n/2}} = \mathcal{O}(t^n). \tag{53}$$

This means that the series for the non-equilibrium Green's functions G_λ in Eq. (51) are well-behaved for small times t (just as the equilibrium Van Hove self-correlation function was) and that by truncating the series one obtains *for small t approximations which can be systematically improved by taking more terms into account.*

We note that in non-equilibrium situations, $\alpha_2 = \kappa_4/(3\kappa_2^2)$ may have a similar behavior as sketched in Figure 1 for the equilibrium α_2. Although a proper numerical test is yet to be performed, this expectation is roughly consistent with numerical results of the Green's function for heat transport:[14–16] In that case the contribution of the non-Gaussian corrections in Eq. (51) were most significant on the sub-picosecond time scale, whereas extrapolation indicated that hydrodynamic-like results may occur for times as short as 2 ps.[15]

In view of the possible application to nano-technology, it is important to understand the behavior on the (sub)picosecond time scale and the related (sub) nanometer length scale over which a particle typically moves at such time scales. The Green's function theory can potentially describe a system on all time scales. The current theorem assures that this theory can at least consistently describe the short time scales, by showing that the expansion of the Green's function is well-behaved. For practical applications, and to know how short the time scales must be for the theorem to apply, it is still necessary to determine the coefficient of the $\mathcal{O}(t^{2n})$ of κ_n, *i.e.* the c_n in Eq. (36). This will require a numerical evaluation of the moments of derivatives of the forces, which we plan to do in the future. The behavior of κ_n at longer time scales will also be investigated in the future.[17]

Acknowledgments

This work was supported by the Office of Basic Energy Sciences of the US Department of Energy under grant number DE-FG-02-88-ER13847.

Appendix

In the text, we needed the following auxiliary theorem to prove the main Theorem.

Theorem A. Let V be a zero mean Gaussian variable and let $\{X_\gamma\}_{\gamma=2\ldots\alpha}$ be a set of functions of V which are polynomials of degree d_γ. Let $\{n_\gamma\}_{\gamma=1\ldots\alpha}$ be a set of nonnegative integers, and let $d = \sum_{\gamma=2}^{\alpha} n_\gamma d_\gamma$. Then if $n_1 > d$ and at least one $n_{\gamma>1} \neq 0$, the following cumulant vanishes:

$$\langle\!\langle V^{n_1} X_2^{n_2} \ldots X_\alpha^{n_\alpha} \rangle\!\rangle = 0. \tag{A.1}$$

while if all $n_{\gamma>1}$ are zero, one has

$$\langle\!\langle V^{n_1} \rangle\!\rangle = \langle\!\langle V^2 \rangle\!\rangle \delta_{n_1 2}. \tag{A.2}$$

Since we have not found a proof of this theorem in the literature, we will give it here, but before we can prove Theorem A, we need four lemmas and the definition of a θ-modified average. This definition will serve, in conjunction with Lemma 1 below, to construct a convenient generating function (which takes the form of a θ-modified cumulant) for the quantities $\langle\!\langle V^{n_1} X_2^{n_2} \dots X_\alpha^{n_\alpha} \rangle\!\rangle$ that occur in Theorem A. Working with this generating function will be more convenient than trying to calculate each $\langle\!\langle V^{n_1} X_2^{n_2} \dots X_\alpha^{n_\alpha} \rangle\!\rangle$ individually. After this generating function has been introduced, Lemma 2 and Lemma 3 are presented and proved, which use the Gaussian nature of V to give properties of averages and θ-modified averages of powers of V which allow one to prove a central polynomial property (Lemma 4) of the generating function of the quantities $\langle\!\langle V^{n_1} X_2^{n_2} \dots X_\alpha^{n_\alpha} \rangle\!\rangle$. This central polynomial property is the main ingredient in the proof of Theorem A at the end of this Appendix.

The definition of θ-modified averages and cumulants is:

Definition. Given the zero-mean Gaussian variable V, the θ-modified average of a variable X is defined as

$$\langle X \rangle_\theta \equiv \frac{\langle e^{\theta V} X \rangle}{\langle e^{\theta V} \rangle} = e^{-\frac{1}{2}\theta^2 \langle V^2 \rangle} \left\langle e^{\theta V} X \right\rangle . \tag{A.3}$$

Similarly, θ-modified moments are defined as the θ-modified averages of powers of variables (*i.e.*, functions of V), and θ-modified cumulants are defined as having the same relation to θ-modified moments as normal cumulants have to normal moments. θ-modified cumulants are therefore also given through the θ-modified cumulant generating function as:

$$\langle\!\langle X_1^{n_1} \dots X_\alpha^{n_\alpha} \rangle\!\rangle_\theta \equiv \prod_{\gamma=1}^{\alpha} \frac{\partial^{n_\gamma}}{\partial(\mathrm{i}k_\gamma)^{n_\gamma}} \log \left\langle \exp \sum_{\gamma=1}^{\alpha} \mathrm{i}k_\gamma X_\gamma \right\rangle_\theta \Bigg|_{k_{1\dots\alpha}=0} . \tag{A.4}$$

The generating function nature of the θ-modified cumulants follows from:

Lemma 1. *(relation between cumulants and θ-modified cumulants)*[3] The θ-modified cumulants of a set of variables $X_1, \dots X_\alpha$ are related to the normal cumulants by

$$\langle\!\langle X_1^{n_1} \dots X_\alpha^{n_\alpha} \rangle\!\rangle_\theta = \begin{cases} \displaystyle\sum_{n=0}^{\infty} \frac{\langle\!\langle V^n X_1^{n_1} \dots X_\alpha^{n_\alpha} \rangle\!\rangle}{n!}\, \theta^n & \text{if at least one } n_\gamma \neq 0, \\ 0 & \text{otherwise.} \end{cases} \tag{A.5}$$

[3]For $\alpha = n_1 = 1$ this lemma coincides with the last exercise of section XVI.3 in Van Kampen.[24]

Proof. The case $n_1 = \cdots = n_\alpha = 0$ is trivial: $\langle\!\langle X_1^{n_1} \ldots X_\alpha^{n_\alpha} \rangle\!\rangle_\theta = \langle\!\langle 1 \rangle\!\rangle_\theta = 0$ since a zeroth cumulant is always zero. For the other cases, we start with the rhs of Eq. (A.5) and use the expression for the cumulants in Eq. (15):

$$\sum_{n=0}^{\infty} \frac{\langle\!\langle V^n X_1^{n_1} \ldots X_\alpha^{n_\alpha} \rangle\!\rangle}{n!} \theta^n$$
$$= \sum_{n=0}^{\infty} \frac{\theta^n}{n!} \frac{\partial^n}{\partial(\mathrm{i}k_0)^n} \prod_{\gamma=1}^{\alpha} \frac{\partial^{n_\gamma}}{\partial(\mathrm{i}k_\gamma)^{n_\gamma}} \log \Big\langle \exp \Big[\mathrm{i}k_0 V + \sum_{\gamma=1}^{\alpha} \mathrm{i}k_\gamma X_\gamma\Big] \Big\rangle \Big|_{k_{0\ldots\alpha}=0} \tag{A.6}$$

We recognize the Taylor series, *i.e.*, that $\sum_{n=1}^{\infty} ([-i\theta]^n/n!)\, \partial^n f(k_0)/\partial k_0^n \Big|_{k_0=0} = f(-i\theta)$ to write this as

$$\sum_{n=0}^{\infty} \frac{\langle\!\langle V^n X_1^{n_1} \ldots X_\alpha^{n_\alpha} \rangle\!\rangle}{n!} \theta^n$$
$$= \prod_{\gamma=1}^{\alpha} \frac{\partial^{n_\gamma}}{\partial(\mathrm{i}k_\gamma)^{n_\gamma}} \log \Big\langle \exp \Big[\theta V + \sum_{\gamma=1}^{\alpha} \mathrm{i}k_\gamma X_\gamma\Big] \Big\rangle \Big|_{k_{1\ldots\alpha}=0} \tag{A.7}$$

Using definition (A.3), this becomes

$$\sum_{n=0}^{\infty} \frac{\langle\!\langle V^n X_1^{n_1} \ldots X_\alpha^{n_\alpha} \rangle\!\rangle}{n!} \theta^n$$
$$= \prod_{\gamma=1}^{\alpha} \frac{\partial^{n_\gamma}}{\partial(\mathrm{i}k_\gamma)^{n_\gamma}} \Big[\log \Big\langle \exp \sum_{\gamma=1}^{\alpha} \mathrm{i}k_\gamma X_\gamma \Big\rangle_\theta + \frac{1}{2}\theta^2 \langle V^2 \rangle \Big] \Big|_{k_{1\ldots\alpha}=0} \tag{A.8}$$

Since we are considering the case that at least one k_γ is nonzero, the contribution from the k_γ-independent $\frac{1}{2}\theta^2\langle V^2\rangle$ vanishes when $\partial/\partial(\mathrm{i}k_\gamma)$ acts on it. The remainder is by definition (A.4) equal to the lhs of Eq. (A.5). □

A consequence of this lemma, *i.e.*, of Eq. (A.5), is that repeated derivatives with respect to θ of $\langle\!\langle X_1^{n_1} \ldots X_\alpha^{n_\alpha} \rangle\!\rangle_\theta$ taken at $\theta = 0$ generate the $\langle\!\langle V^n X_1^{n_1} \ldots X_\alpha^{n_\alpha} \rangle\!\rangle$.

The second lemma concerns the average of a product of powers of V and a single polynomial function of V.

Lemma 2. *(Averages of powers of V times a polynomial in V)* Let X be a variable which is a polynomial function of degree d in the zero mean Gaussian variable V and which is even if d is even and odd if d is odd. The quantities ($n \geq 0$)

$$A_n = \langle V^n X \rangle \tag{A.9}$$

are a) zero in cases where n is odd but d is even and in cases where n is even but d is odd, b) or otherwise given in terms of A_n with lower n as follows. For even $n = 2s$ and $d = 2s^*$, set $\delta = 0$, while for odd $n = 2s + 1$ and $d = 2d^* + 1$, set $\delta = 1$, respectively. Then

$$A_{2s+\delta} = \sum_{s'=0}^{s^*} \frac{(2s-1+2\delta)!!}{(2s'-1+2\delta)!!} \frac{\langle V^2\rangle^{s-s'} A_{2s'+\delta}}{s'!(s^*-s')!} \prod_{\substack{s''=0 \\ s''\neq s'}}^{s^*} (s-s''). \quad \text{(A.10)}$$

Proof. a) Note first that d should be even if n is even and odd if n is odd, respectively, in order to get a non-zero result for A_n, because otherwise, with the even nature of the zero mean Gaussian distribution, the integrand in the average in Eq. (A.9) would be odd in V and yield zero.

b) For even $n = 2s$ and even $d = 2s^*$, *i.e.*, $\delta = 0$, one can write for X

$$X = \sum_{s'=0}^{s^*} C_{s'} V^{2s'} \quad \text{(A.11)}$$

with general coefficients C_s. Using $\langle V^{2p}\rangle = (2p-1)!!\langle V^2\rangle^p$,[23] the result for A_{2s} in terms of the $C_{s'}$ becomes

$$A_{2s} = \sum_{s'=0}^{s^*} C_{s'}\langle V^{2s'+2s}\rangle = \sum_{s'=0}^{s^*} (2s+2s'-1)!!C_{s'}\langle V^2\rangle^{s'+s}. \quad \text{(A.12)}$$

Now let

$$a_s \equiv \frac{A_{2s}}{\langle V^2\rangle^s(2s-1)!!}, \quad \text{(A.13)}$$

which is given, according to Eq. (A.12), by

$$a_s = \sum_{s'=0}^{s^*} (2s+2s'-1)\cdots(2s+1)C_{s'}\langle V^2\rangle^{s'}. \quad \text{(A.14)}$$

The maximum number of factors $(2s + 2s' - 1)$ in this expression is s^*. Since this is the only way in which s enters on the rhs, this implies that a_s is a polynomial in s of degree s^*. The classic Lagrange interpolation formula applied to a polynomial[26] then gives the general expression for the polynomial a_s in terms of its values $a_{s'}$ on the s^*+1 points $s' = 0 \ldots s^*$:[4]

$$a_s = \sum_{s'=0}^{s^*} \frac{a_{s'}}{s'!(s^*-s')!} \prod_{\substack{s''=0 \\ s''\neq s'}}^{s^*} (s-s''). \quad \text{(A.15)}$$

[4]The Lagrange formula is commonly used as an interpolation formula using polynomials for functions whose values are known at a finite number of points. However, in the present case in which the function is known to be a polynomial, the formula is just an exact representation of the function in terms of the values it takes on the $s^* + 1$ points.

Re-substituting Eq. (A.13) in this equation and multiplying by $\langle V^2\rangle^s(2s-1)!!$ yields Eq. (A.10) for $\delta=0$.

The same procedure can be followed for odd values for $n=2s+1$ and $d=2s^*+1$, in which case $\delta=1$. Writing $X=\sum_{s'=0}^{s^*} C_{s'}\, V^{2s'+1}$ gives $\langle V^{2s+1}X\rangle=\sum_{s'=0}^{s^*}(2s+2s'+1)!!C_{s'}\langle V^2\rangle^{s+s'+1}$. The quantities

$$a_s \equiv \frac{A_{2s+1}}{\langle V^2\rangle^s(2s+1)!!} \tag{A.16}$$

are then seen to be once more polynomials in s of degree s^*, and can therefore be expressed by the Lagrange formula in Eq. (A.15). Re-substituting Eq. (A.16) in Eq. (A.15) then leads to Eq. (A.10) for $\delta=1$. □

The third lemma concerns θ-modified averages of polynomials X in V in terms of averages of powers of V times X.

Lemma 3. *(θ-modified average of polynomials in V)* Let X be a variable which is a polynomial of degree d in the zero mean Gaussian variable V. Then the θ-modified average of X is a polynomial in θ of the same degree d and given by

$$\langle X\rangle_\theta = \sum_{\substack{k,s'\geq 0\\ k+2s'\leq d}} \frac{[-\frac{1}{2}\langle V^2\rangle]^{s'}\langle V^k X\rangle}{s'!k!}\,\theta^{k+2s'}. \tag{A.17}$$

Proof. The proof will be in three parts: a, b and c.

a) Consider first the case that X is an even polynomial in V and write its degree as $d=2s^*$. Using Eq. (A.3), expanding $e^{\theta V}$ and using that only even functions of V have a nonzero average, one gets

$$\langle X\rangle_\theta \;=\; e^{-\frac{1}{2}\theta^2\langle V^2\rangle}\sum_{s=0}^{\infty}\frac{\langle V^{2s}X\rangle}{(2s)!}\theta^{2s} \tag{A.18}$$

where part a) of Lemma 2 was used which states that $\langle V^n X\rangle=0$ if n is odd and d is even. Using part b) of Lemma 2, *i.e.* Eq. (A.10) with $\delta=0$ as well, one gets

$$\langle X\rangle_\theta = e^{-\frac{1}{2}\theta^2\langle V^2\rangle}\sum_{s=0}^{\infty}\sum_{s'=0}^{s^*}\frac{(2s-1)!!}{(2s)!}\theta^{2s}\frac{\langle V^2\rangle^{s-s'}\langle V^{2s'}X\rangle}{(2s'-1)!!s'!(s^*-s')!}\prod_{\substack{s''=0\\ s''\neq s'}}^{s^*}(s-s'') \tag{A.19}$$

Noting that $(2s-1)!!/(2s)!=1/(2^s s!)$, this becomes

$$\langle X\rangle_\theta = e^{-\frac{1}{2}\langle V^2\rangle\theta^2}\sum_{s=0}^{\infty}\sum_{s'=0}^{s^*}\frac{[\frac{1}{2}\langle V^2\rangle\theta^2]^s}{s!}\frac{\langle V^{2s'}X\rangle}{\langle V^2\rangle^{s'}(2s'-1)!!s'!(s^*-s')!}\prod_{\substack{s''=0\\ s''\neq s'}}^{s^*}(s-s'') \tag{A.20}$$

In order to get Eq. (A.17), Eq. (A.20) can be rewritten by using for $s' \leq s^*$ [as in the second summation in Eq. (A.20)] the algebraic equality[5]

$$
\begin{aligned}
e^{-\frac{1}{2}\langle V^2\rangle\theta^2} \sum_{s=0}^{\infty} \frac{[\frac{1}{2}\langle V^2\rangle\theta^2]^s}{s!} \prod_{\substack{s''=0\\ s''\neq s'}}^{s^*} (s-s'') \\
= \sum_{s''=0}^{s^*-s'} (-1)^{s''} \left[\frac{1}{2}\langle V^2\rangle\theta^2\right]^{s^*-s''} \frac{(s^*-s')!}{(s^*-s'-s'')!}.
\end{aligned}
\tag{A.21}
$$

Using Eqs. (A.20) and (A.21) and that $(2s-1)!!/(2s)! = 1/(2^s s!)$, one finds

$$
\langle X\rangle_\theta = \sum_{s'=0}^{s^*} \sum_{s''=0}^{s^*-s'} \frac{\langle V^{2s'}X\rangle}{\left\langle\frac{1}{2}V^2\right\rangle^{s'}(2s')!} \frac{(-1)^{s^*+s'+s''}[\frac{1}{2}\langle V^2\rangle\theta^2]^{s^*-s''}}{(s^*-s'-s'')!}. \tag{A.22}
$$

Changing the summation variables from $(s',\, s'')$ to $(s,\, s')$ by replacing s' by s and s'' by s^*-s-s', respectively, gives

$$
\langle X\rangle_\theta = \sum_{\substack{s,s'\geq 0\\ s+s'\leq s^*}} \frac{[-\frac{1}{2}\langle V^2\rangle]^{s'}\langle V^{2s}X\rangle}{s'!(2s)!}\,\theta^{2s+2s'}, \tag{A.23}
$$

which is of the form Eq. (A.17) for an even polynomial X, so the lemma is now proved for this case.

b) Consider next the case that X is an odd polynomial in V of degree $d = 2s^*+1$. Write, using Eq. (A.3) and the part a) of Lemma 2,

$$
\langle X\rangle_\theta = e^{-\frac{1}{2}\theta^2\langle V^2\rangle} \sum_{s=0}^{\infty} \frac{\langle V^{2s+1}X\rangle}{(2s+1)!}\theta^{2s+1} \tag{A.24}
$$

Using part b) of Lemma 2, *i.e* Eq. (A.10) with $\delta = 1$ as well, one gets

$$
\langle X\rangle_\theta = e^{-\frac{1}{2}\theta^2\langle V^2\rangle} \sum_{s=0}^{\infty}\sum_{s'=0}^{s^*} \frac{(2s+1)!!}{(2s+1)!}\theta^{2s+1} \frac{\langle V^2\rangle^{s-s'}\langle V^{2s'+1}X\rangle}{(2s'+1)!!s'!(s^*-s')!} \prod_{\substack{s''=0\\ s''\neq s'}}^{s^*}(s-s'') \tag{A.25}
$$

[5]The proof of the algebraic relation (A.21) for $s' \leq s^*$ goes via induction for both s^* and s'. The start of the induction is the case $s^* = 0$, $s' = 0$, for which Eq. (A.21) is easily verified. Next, one assumes that Eq. (A.21) is satisfied for specific vales $s^* = u^*$ and $s' = u'$ with $u' \leq u^*$. By writing the lhs of Eq. (A.21) as $\exp[-\langle V^2\rangle\theta^2/2]\prod_{s''=0;s''\neq s'}^{s^*}[\theta^2 d/d(\theta^2) - s'']\exp[\langle V^2\rangle\theta^2/2]$, it can be shown that (A.21) then also holds for $s^* = u^*+1$ and $s' = u'$. Thus Eq. (A.21) is proved for values $s' = u' \leq u^* = s^*-1$ but not yet for $s' = s^*$. The latter case can be proved directly in Eq. (A.21) by substituting $s' = s^*$. This completes the proof.

Noting that $(2s+1)!!/(2s+1)! = 1/(2^s s!)$ and performing the same manipulations as in a), one gets

$$\langle X \rangle_\theta = \sum_{\substack{s,s' \geq 0 \\ s+s' \leq s^*}} \frac{[-\frac{1}{2}\langle V^2 \rangle]^{s'} \langle V^{2s+1} X \rangle}{s'!(2s+1)!} \, \theta^{2s+2s'+1}, \tag{A.26}$$

which is of the form Eq. (A.17) for an odd polynomial X, so the lemma is now proved for this case too.

c) To derive the form in Eq. (A.17) for a general polynomial, one splits the general polynomial X up into an even part Y and an odd part Z in V. Using Eqs. (A.23) and (A.26) and using that $\langle Y V^{2s+1} \rangle = \langle Z V^{2s} \rangle = 0$, one obtains straightforwardly Eq. (A.17). □

The next and final lemma we need before we can prove Theorem A concerns θ-modified cumulants of several polynomials in V.

Lemma 4. *(θ-modified cumulants of polynomials in V)* Let $\{X_\gamma\}_{\gamma=1\ldots\alpha}$ be a set of polynomials of degree d_γ in the zero mean Gaussian variable V. Then the θ-modified cumulant $\langle\!\langle X_1^{n_1} \ldots X_\alpha^{n_\alpha} \rangle\!\rangle_\theta$ is a polynomial in θ of the combined degree $d = \sum_{\gamma=1}^{\alpha} n_\gamma d_\gamma$.

Proof. Because the θ-modified cumulants are defined formally in precisely the same way as normal cumulants [*i.e.*, Eq. (A.4) vs. Eq. (15)], the relation Eq. (16) between cumulants and moments applies to the θ-modified cumulants and moments as well. According to that relation, the θ-modified cumulant $\langle\!\langle X_1^{n_1} \ldots X_\alpha^{n_\alpha} \rangle\!\rangle_\theta$ can be expressed as a sum of terms each of which contains a product of the moments $\langle X_1^{\ell_1} \cdots X_\alpha^{\ell_\alpha} \rangle_\theta$ raised to the power $p_{\{\ell\}}$ (where the product is over all possible sets $\{\ell\} = \{l_1, \ldots, l_\alpha\}$ with the restrictions stated in Eq. (16)). Because X_γ is required by the conditions of the lemma to be a polynomial in V of degree d_γ, $X_\gamma^{\ell_\gamma}$ is a polynomial in V of degree $\ell_\gamma d_\gamma$, and the product $X_1^{\ell_1} \cdots X_\alpha^{\ell_\alpha}$ is a polynomial in V of degree $\sum_{\gamma=1}^{\alpha} \ell_\gamma d_\gamma$. According to Lemma 3, each θ-modified moment $\langle X_1^{\ell_1} \cdots X_\alpha^{\ell_\alpha} \rangle_\theta$ is then a polynomial in θ of degree $\sum_{\gamma=1}^{\alpha} \ell_\gamma d_\gamma$. Its $p_{\{\ell\}}$-th power in Eq. (16) is then a polynomial in θ of degree $p_{\{\ell\}} \sum_{\gamma=1}^{\alpha} \ell_\gamma d_\gamma$, and the product (over $\{\ell\}$) that occurs on the rhs of Eq. (16) is of degree $d \equiv \sum_{\{\ell\}} p_{\{\ell\}} \sum_{\gamma=1}^{\alpha} \ell_\gamma d_\gamma$. Since $p_{\{\ell\}}$ is summed over in Eq. (16) with the restriction that $\sum_{\{\ell\}} p_{\{\ell\}} \ell_\gamma = n_\gamma$, the degree d of the expressions $\prod_{\{\ell\}} \langle X_1^{\ell_1} \cdots X_\alpha^{\ell_\alpha} \rangle_\theta^{p_{\{\ell\}}}$ can be rewritten as $d = \sum_{\gamma=1}^{\alpha} n_\gamma d_\gamma$. Each term in the sum over $p_{\{\ell\}}$ on the rhs of Eq. (16) is of this degree d, so the full expression, *i.e.* $\langle\!\langle X_1^{n_1} \ldots X_\alpha^{n_\alpha} \rangle\!\rangle_\theta$, is also a polynomial in θ of degree d. □

Proof of Theorem A.

We can now give the proof of Theorem A. To consider $\langle\langle V^{n_1} X_2^{n_2} \dots X_\alpha^{n_\alpha} \rangle\rangle$ as on the lhs of Eq. (A.1) in the case that at least one $n_{\gamma>1} \neq 0$, we look at its generating function, *i.e.*, $\langle\langle X_2^{n_2} \dots X_\alpha^{n_\alpha} \rangle\rangle_\theta$. According to Eq. (A.5) of Lemma 1, this generating function $\langle\langle X_2^{n_2} \dots X_\alpha^{n_\alpha} \rangle\rangle_\theta$ admits a power series in θ. At the same time, according to Lemma 4 (whose proof required Lemmas 2 and 3), $\langle\langle X_2^{n_2} \dots X_\alpha^{n_\alpha} \rangle\rangle_\theta$ is given by a polynomial in θ of degree $d = \sum_{\gamma=2}^{\alpha} n_\gamma d_\gamma$, so its power series in θ terminates after θ^d. Since these lemmas should be valid for all θ, each coefficient of the $\theta^{n>d}$ terms must be zero, *i.e.*, using Eq. (A.5) of Lemma 1, $\langle\langle V^{n_1} X_2^{n_2} \dots X_\alpha^{n_\alpha} \rangle\rangle / n_1! = 0$ if $n_1 > d$. Since $n_1! \neq 0$, it follows that $\langle\langle V^{n_1} X_2^{n_2} \dots X_\alpha^{n_\alpha} \rangle\rangle = 0$, which is Eq. (A.1) of Theorem A. Finally, for the case $n_2 = \cdots = n_\alpha = 0$, Eq. (A.2) of Theorem A follows from the Gaussian nature of V. □

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