

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

R. van Zon^{1,2} and E. G. D. Cohen¹

Received June 17, 2005; accepted October 17, 2005

Published Online: April 5, 2006

The distribution of the initial short-time displacements of particles is considered for a class of classical systems under rather general conditions on the dynamics and with Gaussian initial velocity distributions, while the positions could have an arbitrary distribution. This class of systems contains canonical equilibrium of a Hamiltonian system as a special case. We prove that for this class of systems the n th order cumulants of the initial short-time displacements behave as the $2n$ -th power of time for all $n > 2$, rather than exhibiting an n th 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.

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

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

1. ON THE STRUCTURE OF THIS PAPER

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

The property can be formulated as a mathematical theorem, which may have more applications than are considered in this paper. Our interest is however

¹ The Rockefeller University, New York, New York 10021

² Current address: Department of Chemistry, University of Toronto, Toronto, Canada M5S 3H6; e-mail: rzon@chem.utoronto.ca

mainly in its physical applications. Since the general theorem and its proof are best formulated in a rather abstract way which is not necessary for the currently known physical applications, the paper is split up into a physical part (Part 2) containing the physical formulation of the Theorem and its applications, and a mathematical part (Part 3) containing the general mathematical formulation of the Theorem and its proof.

These two parts are further subdivided into sections. In Sec. 2.1 the physical motivation for studying particle displacements is given. In Sec. 2.2 we introduce the physical systems that will be considered. Section 2.3 gives the necessary definitions to be able to treat the cumulants of the particle displacements. We state the Theorem in physical terms in Sec. 2.4 and discuss its physical applications in Sec. 2.5.

As for the mathematical Part 3 of the paper, in Sec. 3.1, we give the general definition of cumulants of any number of random variables and discuss some of their properties, while in Sec. 3.2 we present the Theorem in its full mathematical generality. In Sec. 3.3 we prove the Theorem. In the proof we need an auxiliary theorem concerning Gaussian distributed variables whose proof is postponed to the Appendix. Some coefficients occurring in the Theorem are worked out in Sec. 3.4.

We end with conclusions, which are followed by the Appendix.

2. PHYSICAL PART

2.1. Introduction

Our motivation to consider the displacements of particles originates from trying to describe the behavior of non-equilibrium systems on all time scales using the so-called Green's function theory, introduced by J. M. Kincaid.⁽¹³⁾ 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 one expects that they can describe the system on more than just long time and length scales, in particular also 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 studying the picosecond and sub-picosecond time scales could also be relevant for nanotechnology.

For mass transport in multi-component fluids,^(13,17) the Green's functions $G_\lambda(\mathbf{r}, \mathbf{r}', t)$ have the physical interpretation of being the probability that a single

particle of component λ is at a position \mathbf{r} at time t given that it was at a position \mathbf{r}' at time zero. At time zero the system is not in equilibrium, in fact, a class of far-from-equilibrium situations has been studied in this context.^(14–17) Given this interpretation, it is clear that the displacements of single particles are the central quantities in the Green's function theory.

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 $G_s(\mathbf{r} - \mathbf{r}', t)$.^(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) the so-called cumulants of the particle displacements (defined in Sec. 2.3 below) have been studied by Schofield⁽²⁾ and Sears,⁽⁷⁾ among others. 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} which can be measured and is defined as

$$F_s(k, t) = \langle e^{i\mathbf{k}\hat{\mathbf{k}}\cdot[\mathbf{r}_1(t) - \mathbf{r}_1(0)]} \rangle_{eq} = \langle e^{ik\Delta x_1(t)} \rangle_{eq}, \quad (2.1)$$

where $\mathbf{k} = k\hat{\mathbf{k}}$ is a wave vector with length k and direction $\hat{\mathbf{k}}$ (a unit vector), $\mathbf{r}_1(t)$ the position of a (single) particle at time t and $\langle \rangle_{eq}$ 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) $\log\langle \exp[ikA] \rangle$ is the cumulant generating function for the random variable A , so we see from (2.1) 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 $\sum_{n=1}^{\infty} \kappa_n (ik)^n / n!$ where κ_n is the n th 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)

$$F_s(k, t) = \exp \sum_{n=1}^{\infty} \frac{\kappa_n}{n!} (ik)^n. \quad (2.2)$$

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. We note that (2.2) also shows that the cumulants could be obtained experimentally by measuring $F_s(k, t)$ via small k (“small angle”) incoherent neutron scattering and fitting the logarithm of the result to a power series in k . In Sec. 2.5 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.

In the context of incoherent neutron scattering, it has been noted by Schofield⁽²⁾ and Sears⁽⁷⁾ that the cumulants κ_n of the displacement of a

particle in a time t in a fluid in equilibrium with a smooth interparticle 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. These results suggested for equilibrium systems with smooth potentials a behavior as the $2n$ -th power in t for κ_n when $n > 2$ in general, 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 $\mathcal{O}(t^{2n-1})$,³ should *vanish*. The question we address here is whether this is indeed general for smooth potentials.

In fact in this paper we shall show that under quite general conditions, the main one being that in the initial ensemble, the velocities have a multi-variate Gaussian distribution⁽²⁴⁾ and are statistically independent of the positions, one can prove a very general theorem to be presented in the next part. This theorem implies, among other things, that for a many particle system in which the (interparticle as well as external) forces are independent of the velocities, the n th order cumulants of the displacement are indeed $\mathcal{O}(t^{2n})$ for $n > 2$ and $\mathcal{O}(t^n)$ for $n \leq 2$. This confirms the above stated expectation, but extends it to a restricted class of non-equilibrium situations as well, as we will show.

2.2. Class of Physical Systems

In this part we will restrict ourselves to the following class of systems (the Theorem in Part 2 of the paper concerns a more general class). Consider N point particles in three dimensions⁴ whose positions and velocities are denoted by the three-dimensional vectors \mathbf{r}_i and \mathbf{v}_i , respectively, and whose masses are m_i , where $i = 1 \dots N$. The time evolution of the particles is governed by

$$\dot{\mathbf{r}}_i = \mathbf{v}_i \tag{2.3}$$

³ Everywhere in this paper “up to $\mathcal{O}(t^\alpha)$ ” means “up to and including $\mathcal{O}(t^\alpha)$.”

⁴ Other dimensionalities work just as well.

$$\dot{\mathbf{v}}_i = \mathbf{F}_i(\mathbf{r}^N, t)/m_i, \quad (2.4)$$

where \mathbf{F}_i is the force acting on particle i , which is supposed to be a smooth function of the time t and of \mathbf{r}^N , which is the collection of all positions \mathbf{r}_i . Likewise, \mathbf{v}^N will denote the collection of all velocities \mathbf{v}_i .

We consider an ensemble of such systems. In the ensemble, the initial probability distribution $\mathcal{P}(\mathbf{r}^N, \mathbf{v}^N)$ of the positions and the velocities of the particles is such that the velocities each have a Gaussian distribution and are statistically independent of the positions, i.e.,⁵

$$\mathcal{P}(\mathbf{r}^N, \mathbf{v}^N) = f(\mathbf{r}^N) \prod_{i=1}^N \left[\left(\frac{\beta_i m_i}{2\pi} \right)^{3/2} \exp \left(-\frac{1}{2} \beta_i m_i |\mathbf{v}_i - \mathbf{u}_i|^2 \right) \right]. \quad (2.5)$$

where \mathbf{u}_i is the average of the initial velocity \mathbf{v}_i and β_i are positive “inverse temperature”-like variables. In (2.5), the $f(\mathbf{r}^N)$ denotes a general probability distribution function of the initial positions of the particles. While the distribution function in (2.5) can describe both equilibrium and non-equilibrium situations, it always shares with the equilibrium distribution the Gaussian dependence on the velocities, which is in fact crucial for the Theorem below to hold.

We stress that the forces \mathbf{F}_i in (2.5) are independent of the velocities, but may depend on the positions \mathbf{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 $\mathbf{F}_i(\mathbf{r}^N, t)$, but also Lennard-Jones-like forces are allowed provided the distribution of the positions $f(\mathbf{r}^N)$ assigns a vanishing probability to the particles to be at zero distance of one another, which is the singular point of the Lennard-Jones-like potential at which it is not smooth.

Canonical equilibrium for a single or multi-component fluid is just a special case of these systems. In that case, one has $\mathbf{u}_i = 0$, $\beta_i = \beta$, $\mathbf{F}_i = -\partial U/\partial \mathbf{r}_i$ and $f(\mathbf{r}^N) \propto \exp[-\beta U(\mathbf{r}^N)]$, where $U(\mathbf{r}^N)$ is the potential energy function of the system.

The probability distribution functions of the form (2.5) in which each particle has its own mean velocity \mathbf{u}_i and “inverse temperature” β_i , may seem at first 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/or temperatures of the different components could be selected physically e.g. by having two vessels with different substances at different temperatures with a divider which is opened at $t = 0$, or by means of a laser (or perhaps even a neutron beam) applied at

⁵ The expression in (2.5) is not the most general Gaussian distribution for \mathbf{v}^N . While the Theorem in Part 3 of the paper allows any multivariate Gaussian distribution of the velocities, we have in fact not found any physical applications for that yet.

$t = 0$, 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” due to the recoil energy.⁽¹⁰⁾ To what extent such techniques could ensure the Gaussianity of the velocity distribution is a technical matter that we will not go into here.

2.3. Definition of Moments and Cumulants

In this paper, when we speak of a random variable, we mean a function of the positions \mathbf{r}^N and the velocities \mathbf{v}^N and possibly the time t . All physical quantities are variables of this kind. For such variables $A(\mathbf{r}^N, \mathbf{v}^N, t)$, the average with respect to the distribution function $\mathcal{P}(\mathbf{r}^N, \mathbf{v}^N)$ will be denoted by

$$\langle A \rangle = \int d\mathbf{r}^N d\mathbf{v}^N \mathcal{P}(\mathbf{r}^N, \mathbf{v}^N) A(\mathbf{r}^N, \mathbf{v}^N, t). \quad (2.6)$$

Throughout the paper, A 's will denote general variables.

We define $\Delta\mathbf{r}_i(t) = (\Delta x_i(t), \Delta y_i(t), \Delta z_i(t))$ as the displacement of particle i in time t , where $i = 1 \dots N$ and the time dependence is suppressed for brevity. The n th moment⁶ of $\Delta x_i(t)$ is the average of its n th power, and is denoted as

$$\mu_n \equiv \langle \Delta x_i^n(t) \rangle, \quad (2.7)$$

where the dependence on i and t on the left-hand side (lhs) has been suppressed. In the following we will also suppress the t dependence in Δx_i . The cumulants of Δx_i ,⁶ denoted by κ_n , are equal to the moments μ_n with certain factorizations of them subtracted and thus sensitive to the correlations of Δx_i . Their precise definition is via the cumulant generating function^(23,24)

$$\Phi(k) \equiv \log \langle \exp[ik \Delta x_i] \rangle = \sum_{n=1}^{\infty} \frac{\kappa_n}{n!} (ik)^n. \quad (2.8)$$

from which the κ_n follow as

$$\kappa_n \equiv \left. \frac{\partial^n \Phi}{\partial (ik)^n} \right|_{k=0}. \quad (2.9)$$

An alternative notation for the cumulants, which is more analogous to (2.7) and which is especially convenient in the case of several variables, is⁽²⁴⁾

$$\langle\langle \Delta x_i^{[n]} \rangle\rangle \equiv \kappa_n. \quad (2.10)$$

⁶ Although the moments μ_n and cumulants κ_n are really the “moments and cumulants of the probability distribution function of $\Delta x_i(t)$,” we will refer to them simply as the “moments and cumulants of $\Delta x_i(t)$.”

We stress here that the superscript $[n]$ is not a power. Furthermore, we will follow the convention that the superscript will not be denoted if $n = 1$, i.e., $\langle\langle \Delta x_i \rangle\rangle \equiv \langle\langle \Delta x_i^{[1]} \rangle\rangle$ (which is also equal to $\kappa_1 = \langle \Delta x_i \rangle$).

The cumulant generating function in (2.8) can be expressed in terms of the moments μ_n since $\Phi(k) = \log(\exp[ik\Delta x_i]) = \log[1 + \sum_{n=1}^{\infty} (ik)^n \mu_n/n!]$. 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 powers of the second term inside the logarithm. This gives, somewhat formally,

$$\kappa_n = -n! \sum_{\substack{\{p_\ell \geq 0\} \\ \sum_{\ell=1}^{\infty} \ell p_\ell = n}} \left(\sum_{\ell=1}^{\infty} p_\ell - 1 \right)! \prod_{\ell=1}^{\infty} \frac{(-\mu_\ell/\ell!)^{p_\ell}}{p_\ell!} \quad (2.11)$$

For instance, for the first few κ_n , (2.11) 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)

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 their ‘‘frequencies of occurrence’’ p_ℓ) add up to n .

Apart from the cumulants κ_n of the single variable Δx_i , we will also need the general definition of cumulants which applies to the displacement of the same particle in different spatial directions as well as the displacements of different particles. Like for the cumulants of a single particle’s displacement, the expressions for the general cumulants are moments with factored forms subtracted, e.g.

$$\langle\langle \Delta x_1; \Delta x_2 \rangle\rangle = \langle \Delta x_1 \Delta x_2 \rangle - \langle \Delta x_1 \rangle \langle \Delta x_2 \rangle \quad (2.12)$$

$$\begin{aligned} \langle\langle \Delta x_1; \Delta y_1; \Delta z_1 \rangle\rangle &= \langle \Delta x_1 \Delta y_1 \Delta z_1 \rangle - \langle \Delta x_1 \rangle \langle \Delta y_1 \Delta z_1 \rangle - \langle \Delta x_1 \Delta y_1 \rangle \langle \Delta z_1 \rangle \\ &\quad - \langle \Delta x_1 \Delta z_1 \rangle \langle \Delta y_1 \rangle + 2 \langle \Delta x_1 \rangle \langle \Delta y_1 \rangle \langle \Delta z_1 \rangle \end{aligned} \quad (2.13)$$

$$\begin{aligned} \langle\langle \Delta x_1^{[2]}; \Delta y_1^{[2]} \rangle\rangle &= \langle \Delta x_1^2 \Delta y_1^2 \rangle - \langle \Delta x_1^2 \rangle \langle \Delta y_1^2 \rangle - 2 \langle \Delta x_1 \Delta y_1 \rangle^2 \\ &\quad - 2 \langle \Delta x_1 \rangle \langle \Delta x_1 \Delta y_1^2 \rangle - 2 \langle \Delta x_1^2 \Delta y_1 \rangle \langle \Delta y_1 \rangle \\ &\quad + 8 \langle \Delta x_1 \rangle \langle \Delta x_1 \Delta y_1 \rangle \langle \Delta y_1 \rangle - 6 \langle \Delta x_1 \rangle^2 \langle \Delta y_1 \rangle^2. \end{aligned} \quad (2.14)$$

Here, the semi-colons are inserted to avoid ambiguity and to make it explicit that the expressions inside the double angular brackets are not to be multiplied. This is different from the notation for the multivariate cumulants used by Van Kampen⁽²⁴⁾ who denotes the above cumulants as $\langle\langle \Delta x_1 \Delta x_2 \rangle\rangle$, $\langle\langle \Delta x_1 \Delta y_1 \Delta z_1 \rangle\rangle$ and $\langle\langle \Delta x_1^2 \Delta y_1^2 \rangle\rangle$, respectively, which would suggest that the expressions inside the double brackets are products of powers, which they are not.

The general definition of the multivariate cumulants will be given in (3.9) in Sec. 3.1 (where we will also show how the various prefactors are determined) and can also be found in refs. 23 and 24.

2.4. The Theorem in Physical Terms

For the class of physical systems described above, the general and somewhat formal Theorem in Part 3 of the paper states that, in a less abstract physical notation

$$\begin{aligned} & \langle\langle \Delta x_1^{[n_{1x}]}, \Delta y_1^{[n_{1y}]}, \Delta z_1^{[n_{1z}]}, \Delta x_2^{[n_{2x}]}, \Delta y_2^{[n_{2y}]}, \Delta z_2^{[n_{2z}]}, \dots \rangle\rangle \\ &= \begin{cases} c_{\{n_{i\eta}\}} t^n + \mathcal{O}(t^{n+1}) & \text{if } n \leq 2 \\ c_{\{n_{i\eta}\}} t^{2n} + \mathcal{O}(t^{2n+1}) & \text{if } n > 2, \end{cases} \end{aligned} \quad (2.15)$$

where $n_{i\eta}$ are non-negative numbers (some may be zero), $i = 1 \dots N$, $\eta = x, y$ or z and

$$n = \sum_{i=1}^N \sum_{\eta=x,y,z} n_{i\eta} \quad (2.16)$$

is the *order of the cumulant* on the lhs of (2.15).

Note that the cumulants κ_n that occur in the expansion of the Van Hove self-correlation function are special cases of these n th order cumulants, i.e., we can write

$$\kappa_n = \langle\langle \Delta x_i^{[n]} \rangle\rangle = \begin{cases} c_n t^n + \mathcal{O}(t^{n+1}) & \text{for } n \leq 2 \\ c_n t^{2n} + \mathcal{O}(t^{2n+1}) & \text{for } n > 2. \end{cases} \quad (2.17)$$

Section 3.4 contains the expressions for the c_n and the $c_{\{n_{i\eta}\}}$.

We stress once more that on the basis of the connection between the cumulants and the moments (2.11), only an $\mathcal{O}(t^n)$ scaling of the n th order cumulants is to be expected, so that this is a nontrivial theorem. The result in (2.17) generalizes the results of Schofield⁽²⁾ and Sears⁽⁷⁾ who found that for an equilibrium liquid, $\kappa_2 = \mathcal{O}(t^2)$ while $\kappa_4 = \mathcal{O}(t^8)$ and $\kappa_6 = \mathcal{O}(t^{12})$. The results in (2.15) and (2.17) hold, however, also out of equilibrium as long as the initial distribution of the particle velocities is Gaussian and statistically independent of the particles' positions.

2.5. Applications

We will now discuss a number of physical applications of the Theorem in (2.15)–(2.17) just presented.

2.5.1. 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 $G_s(r, t)$ (with $r = |\mathbf{r} - \mathbf{r}'|$), which is the Fourier inverse of the incoherent scattering function $F_s(k, t)$.^(1,8–12) If the length of the wave vector k in $F_s(k, t)$ is small, then according to (2.2) $F_s(k, t) \approx \exp[-\kappa_2 k^2 / 2]$, 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 $F_s(k, t) = \exp \sum_n \kappa_n (ik)^n / n!$ in (2.2) to the form

$$F_s(k, t) = e^{-\frac{1}{2}\kappa_2 k^2} \left[1 + \sum_{\substack{n=4 \\ n \text{ even}}}^{\infty} b_n k^n \right] \quad (2.18)$$

using that in equilibrium odd cumulants are zero. For $n \geq 4$, the coefficients b_n are given by⁽¹⁷⁾

$$b_n = \sum_{\substack{\{p_\ell \geq 0; \ell \text{ even}\} \\ \sum_{\ell=4, \ell \text{ even}}^{\infty} \ell p_\ell = n}} \prod_{\ell=4}^{\infty} \left[\frac{1}{p_\ell!} \left(\frac{\kappa_\ell}{\ell!} \right)^{p_\ell} \right]. \quad (2.19)$$

For example, $b_4 = \kappa_4/4!$, $b_6 = \kappa_6/6!$, $b_8 = (\kappa_8 + 35\kappa_4^2)/8!$. Fourier inverting the resummed form of $F_s(k, t)$ leads to

$$G_s(r, t) = \frac{e^{-w^2}}{\sqrt{2\pi\kappa_2}} \left[1 + \sum_{\substack{n=4 \\ n \text{ even}}}^{\infty} \frac{b_n}{(2\kappa_2)^{n/2}} H_n(w) \right]. \quad (2.20)$$

Here H_n is the n th Hermite polynomial and the dimensionless $w \equiv r/\sqrt{2\kappa_2}$. We note that the series in (2.20) appears to have a fairly rapid convergence.⁽⁶⁾ Taking just the first few terms would give

$$G_s(r, t) = \frac{e^{-w^2}}{\sqrt{2\pi\kappa_2}} \left[1 + \frac{\kappa_4}{4!4\kappa_2^2} H_4(w) + \frac{\kappa_6}{6!8\kappa_2^3} H_6(w) + \dots \right]. \quad (2.21)$$

The Theorem in (2.17) provides a justification for the expansion in (2.20) of the self part of the Van Hove function G_s for short times t in the following way. As (2.19) and (2.20) show, the cumulants $\kappa_{n \geq 4}$ give, via the b_n , 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 (2.20), so also $H_n(w) = \mathcal{O}(1)$. Its prefactor in (2.20) is, however, t -dependent through $b_n/(2\kappa_2)^{n/2}$. Given the relation between b_n and κ_n in (2.19) 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 $b_{n>2} = \mathcal{O}(t^{2n})$. Since $\kappa_2 = \mathcal{O}(t^2)$, we obtain

$$\frac{b_n}{(2\kappa_2)^{n/2}} = \mathcal{O}(t^n). \quad (2.22)$$

This means that the series in (2.20) is well-behaved for small times t , in that each next term is smaller than the previous one, and that by truncating the

series⁷ 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 (2.20) would have been of the same order.

b) An expansion of a similar form as (2.20) 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 applications 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) We note that while supercooled liquids and glasses are not in true equilibrium (for that would be the solid phase), they do have a Gaussian velocity distribution ‘inherited’ from the fluid phase.

Given the present interest in these non-Gaussian parameters α_n , we will now compare them with the cumulants κ_n . The non-Gaussian parameters α_n are defined in terms of the distance $\Delta R = \sqrt{\Delta x^2(t) + \Delta y^2(t) + \Delta z^2(t)}$ traveled by any particle in time t in a three dimensional fluid, as⁽⁴⁾

$$\alpha_n \equiv \frac{\langle \Delta R^{2n} \rangle}{\langle \Delta R^2 \rangle^n (2n+1)!! / 3^n} - 1. \quad (2.23)$$

For isotropic fluids, $\langle \Delta R^{2n} \rangle = (2n+1)\langle \Delta x^{2n}(t) \rangle = (2n+1)\mu_{2n}$, so that (2.23) can then be written as

$$\alpha_n = \frac{\mu_{2n} - (2n-1)!!\mu_2^n}{(2n-1)!!\mu_2^n}. \quad (2.24)$$

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 (2.24) 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 (2.11) have all possible factored terms subtracted. Using (2.24) and the inverse of the relation between κ_n and μ_n in (2.11) (which can be found by using the generating functions), it is possible to express the α_n in terms of κ_n as

$$\alpha_n = n! \sum_{\substack{0 \leq p_\ell < n \\ \sum_{\ell=1}^{\infty} \ell p_\ell = n}} \prod_{\ell=1}^{\infty} \left[\frac{1}{p_\ell!} \left(\frac{2^\ell \kappa_{2\ell}}{(2\ell)! \kappa_2^\ell} \right)^{p_\ell} \right]. \quad (2.25)$$

⁷When truncating, terms that are kept have to include not just the leading order in t , but at least all terms up to $\mathcal{O}(t^k)$ if terms up to H_k are kept. In numerical approaches it is possible to retain the full terms.

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

$$\alpha_2 = \frac{1}{3} \frac{\kappa_4}{\kappa_2^2} \quad (2.26)$$

$$\alpha_3 = \frac{\kappa_4}{\kappa_2^2} + \frac{1}{15} \frac{\kappa_6}{\kappa_2^3} \quad (2.27)$$

The Theorem in (2.17) says that for small times t , $\kappa_2 = \mathcal{O}(t^2)$ and $\kappa_{n>2} = \mathcal{O}(t^{2n})$, so that $\kappa_{2n}/\kappa_2^n = \mathcal{O}(t^{2n})$. According to (2.25), 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 (2.25) and the Theorem, one can derive straightforwardly that the dominant term for small t in (2.25) is the one with $p_1 = n - 2$, $p_2 = 1$ and $p_{\ell>2} = 0$, which leads to

$$\alpha_n \sim \frac{n(n-1)}{2} \alpha_2 \quad (2.28)$$

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 for small t .^(4,8)

In terms of the α_n , the expansion of G_s in (2.21) becomes, with the help of (2.26),

$$G_s(r, t) = \frac{e^{-w^2}}{\sqrt{2\pi\kappa_2}} \left[1 + \frac{3\alpha_2}{4!4} H_4(w) + \frac{15(\alpha_3 - 3\alpha_2)}{6!8} H_6(w) + \dots \right]. \quad (2.29)$$

Although formally equivalent to (2.21), for small t , (2.29) is somewhat less convenient, because one cannot see right away that the last term (involving H_6) is $\mathcal{O}(t^6)$ rather than $\mathcal{O}(t^4)$, as one may naively suspect from $\alpha_2 = \mathcal{O}(t^4)$ and $\alpha_3 = \mathcal{O}(t^4)$. Thus, a cancellation between the leading orders of α_3 and $3\alpha_2$ has to take place, which, especially using a numerical evaluation of the α_n , may be hard to obtain. On the other hand, in (2.21), this cancellation is automatic.

We note that, somewhat surprisingly, the data of Rahman also show that the relation between α_n and α_2 in (2.28) is still approximately satisfied for larger times.⁽⁴⁾ This seems even true for hard spheres.⁽²⁶⁾ Thus the higher order 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 (2.20), although it may be well-behaved for small enough t , it is not known up to what time this remains so. Since $b_n = \mathcal{O}(t^{2n})$

only to leading order in t , there is a point in time after which the $\mathcal{O}(t^{2n})$ term is no longer a good approximation, and this may be related to the point at which the series in (2.20) is no longer guaranteed to be useful. Rahman investigated α_2 (as well as α_3 and α_4) numerically for a model of liquid argon (temperature 94 K, density $1.4 \cdot 10^3 \text{ kg/m}^3$).⁽⁴⁾ (See also ref. 8 for a broader overview.) 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 $t \approx 0.1\text{--}0.2$ ps. At that point the curve shoots up rapidly, leading to a large ‘‘hump,’’ which lasts up to about 10 ps (or perhaps somewhat below that), after which it starts to decrease to zero.

Although somewhat outside the scope of this paper, we would like to give a possible interpretation of the numerical results sketched in Figure 1 for moderate and high densities. 1) The flat behavior of α_2 near $t = 0$ corresponds to the $\mathcal{O}(t^4)$ behavior as given by the Theorem in (2.17). 2) 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 may well be 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.⁽²⁷⁾ Thus at $t = t_s$ the scaling $\mathcal{O}(t^4)$ for α_2 ought to go over to $\mathcal{O}(|t|)$, or in fact, because of the duration t_s of the ‘collision,’ to $\mathcal{O}(|t - t_s|)$, which would require the kind of sharp increase observed by Rahman at ≈ 0.1 ps. 3) While a persistence of non-Gaussianity occurs already in dilute systems,⁽²⁶⁾ this is due to a different mechanism than in

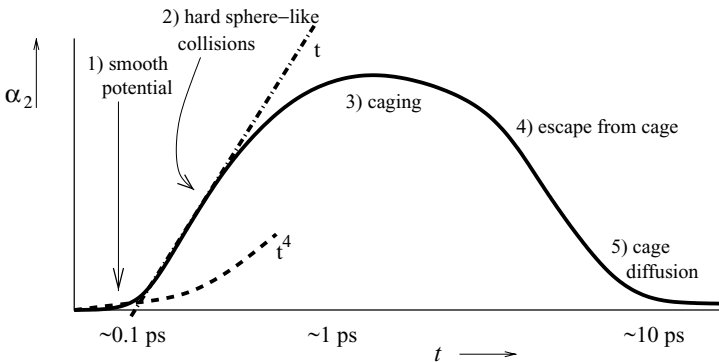


Fig. 1. Sketch of the behavior of the non-Gaussian parameter $\alpha_2 = \kappa_4/(3\kappa_2^2)$ for regular liquids in equilibrium in different time regimes (based on fig. 7 in ref. 4 and fig. 4.11 in ref. 8), with our physical interpretation for each regime.

denser systems, where it comes about because the particle is trapped in a “cage” formed by its neighboring particles, with which it has repeated and correlated collisions. This effect is dominant at high densities.⁽¹⁹⁾ 4) The decay of α_2 to zero indicates that the motion becomes Gaussian and presumably sets in (for dense systems) when 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.⁽²⁸⁾ 5) 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. The precise mechanism of the long-time behavior at low densities falls outside the scope of this paper.

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 particles escape their cages. But the Theorem in (2.15)–(2.17) has nothing to say about α_2 on that time scale.

2.5.2. Local Equilibrium Systems

As a first example of a non-equilibrium system to which the theorem may apply, we consider a fluid not too far from equilibrium, such that it has initially roughly an equilibrium distribution except that the temperature, fluid velocity and density are spatially dependent, i.e., it is in local equilibrium. The class of initial distributions in (2.5) does not seem to be of that form, and indeed, if β_i and \mathbf{u}_i are allowed to vary with \mathbf{r}_i , then the proof as given in the next part of this paper, runs into difficulties. Nonetheless, one can construct distributions of the form (2.5) which physically describe precisely the local equilibrium situation. Imagine dividing the physical volume \mathcal{V} into M cells of equal size and assigning to each cell a a temperature β_a , a fluid velocity \mathbf{u}_a and a density n_a . The particles of the system are divided up as well, putting $N_a = n_a \mathcal{V} / M$ 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 $f(\mathbf{r}^N)$ in (2.5) such that the chance for these particles to be outside their cell is zero. Next, we set all the β_i and \mathbf{u}_i of the particles in cell a equal to β_a and \mathbf{u}_a . If the cells are big enough so that fluctuations in the number of particles can be neglected, this situation describes local equilibrium just as well as spatially dependent $\beta(\mathbf{r}_i)$ and $\mathbf{u}(\mathbf{r}_i)$ can, and for this constructed local equilibrium, the Theorem in (2.15) holds.

2.5.3. Out-of-Equilibrium Phenomena on Very Short Time Scales

In this section, we consider somewhat more general out-of-equilibrium systems, namely those that start at $t = 0$ with a Gaussian velocity distribution. The distribution of the positions of the particles is allowed to be very different from that in equilibrium, however.

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 here in one dimension as:⁽¹⁷⁾

$$n_\lambda(x, t) = \int dx' G_\lambda(x, x', t) n_\lambda(x', 0), \quad (2.30)$$

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 (2.20), as

$$G_\lambda(x, x', t) = \frac{e^{-w^2}}{\sqrt{2\pi\kappa_2}} \cdot \left[1 + \sum_{n=3}^{\infty} \frac{b_n}{(2\kappa_2)^{n/2}} H_n(w) \right] \quad (2.31)$$

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

$$b_n = \sum_{\{p_\ell \geq 0\}} \prod_{\ell=3}^{\infty} \left[\frac{1}{p_\ell!} \left(\frac{\kappa_\ell}{\ell!} \right)^{p_\ell} \right]. \quad (2.32)$$

$\sum_{\ell=3}^{\infty} \ell p_\ell = n$

Some examples are: $b_3 = \kappa_3/3!$, $b_4 = \kappa_4/4!$, $b_5 = \kappa_5/5!$ and $b_6 = (\kappa_6 + 10\kappa_3^2)/6!$. These equations are non-equilibrium generalizations of the equations for the equilibrium Van Hove self-correlation function in (2.20) and (2.19), respectively. However, different from the case of the Van Hove self-function, in the Green's function theory, the κ_n , and thus the b_n through (2.32), 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 (2.5) 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 (2.5), with $f(\mathbf{r}^N) \rightarrow f'(\mathbf{r}^N) = \delta(x_i - x')f(\mathbf{r}^N)$, where x' is just a parameter. Thus, as long as we restrict ourselves to systems with Gaussian initial velocity distributions, the Theorem in (2.17) still applies. Note that the $f(\mathbf{r}^N)$ may describe any non-equilibrium distribution of the positions of the particles.

The Gaussian factor in (2.31) suggests as before that typical values of w are $\mathcal{O}(1)$, so $H_n(w) = \mathcal{O}(1)$. Its prefactor in (2.31) is $b_n/(2\kappa_2)^{n/2}$. Using the Theorem in (2.17) that $\kappa_n = \mathcal{O}(t^{2n})$ and the relation between b_n and κ_n in (2.32) it is easy to see that also $b_n = \mathcal{O}(t^{2n})$. Since $\kappa_2 = \mathcal{O}(t^2)$, we obtain

$$\frac{b_n}{(2\kappa_2)^{n/2}} = \mathcal{O}(t^n). \quad (2.33)$$

This means that, for these systems, the series for the non-equilibrium Green's functions G_λ in (2.31) 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. This statement is in fact not restricted to the one-dimensional case of the Green's functions discussed here; the three-dimensional version, for which the b_n become tensors and which will be presented elsewhere,⁽¹⁷⁾ exhibits—when the general formulation in (2.15) is used—the same scaling with t of the subsequent terms in the series for the Green's functions.

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 (2.31) (involving the Hermite polynomials) were most significant on the sub-picosecond time scale, whereas extrapolation indicated that hydrodynamic-like results may occur for times possibly as short as 2 ps.⁽¹⁵⁾

In view of the possible application to nano-technology, it is important to understand the behavior on very short time scales and the related small length scales 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 very 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 (2.17) (cf. Sec. 3.4). 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, with special attention to the question whether the Green's functions give hydrodynamic behavior for long times.⁽¹⁷⁾

3. MATHEMATICAL PART

In this part, we present (Sec. 3.2) and prove (Sec. 3.3) the Theorem in its most general, mathematical form.

In the mathematical formulation of the Theorem, as well as in its proof, it is convenient to adopt a different notation than the one introduced in Part 2. Since from a mathematical point of view it does not matter whether different degrees of freedom are associated with different spatial directions or with different particles, the mathematical notation will treat all these degrees of freedom on the same footing. This can be achieved by calling the x component of particle one the first degree of freedom, its y component the second, its z component the third, and then the x component of particle two the fourth degree of freedom, etc. The total number of degrees of freedom is then $\mathcal{N} = 3N$.

One can achieve the goal of describing all degrees of freedom in the same way by associating with each degree of freedom a (generalized) position r_i and a (generalized) velocity v_i , and rewriting the three dimensional real positions \mathbf{r}_i and velocities \mathbf{v}_i by using the mapping

$$\mathbf{r}_1 \rightarrow \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}, \quad \mathbf{r}_2 \rightarrow \begin{pmatrix} r_4 \\ r_5 \\ r_6 \end{pmatrix}, \quad \dots \quad (3.1)$$

and similar for the velocities and the average velocities, i.e.,

$$\mathbf{v}_1 \rightarrow \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}, \quad \mathbf{v}_2 \rightarrow \begin{pmatrix} v_4 \\ v_5 \\ v_6 \end{pmatrix}, \quad \dots \quad (3.2)$$

$$\mathbf{u}_1 \rightarrow \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix}, \quad \mathbf{u}_2 \rightarrow \begin{pmatrix} u_4 \\ u_5 \\ u_6 \end{pmatrix}, \quad \dots \quad (3.3)$$

respectively.

Applying this mapping on the equations of motion (2.3) and (2.4), one finds that the generalized positions r_i and velocities v_i (collectively denoted by $r^{\mathcal{N}}$ and $v^{\mathcal{N}}$ respectively) satisfy

$$\dot{r}_i = v_i \quad (3.4)$$

$$\dot{v}_i = a_i(r^{\mathcal{N}}, t) \quad (3.5)$$

where the $a_i(r^{\mathcal{N}}, t)$ are the accelerations which follow from the mapping

$$\frac{\mathbf{F}_1(\mathbf{r}^{\mathcal{N}}, t)}{m_1} \rightarrow \begin{pmatrix} a_1(r^{\mathcal{N}}, t) \\ a_2(r^{\mathcal{N}}, t) \\ a_3(r^{\mathcal{N}}, t) \end{pmatrix}, \quad \frac{\mathbf{F}_2(\mathbf{r}^{\mathcal{N}}, t)}{m_2} \rightarrow \begin{pmatrix} a_4(r^{\mathcal{N}}, t) \\ a_5(r^{\mathcal{N}}, t) \\ a_6(r^{\mathcal{N}}, t) \end{pmatrix}, \quad \dots \quad (3.6)$$

We note that a possible interpretation of this formulation is that of \mathcal{N} “particles” moving in just one spatial dimension. This convenient picture, in which each r_i and v_i may be seen as the one-dimensional position and velocity of a

“particle” i respectively, will be used below, even though the system is not really one-dimensional. Cumulants that in the physical formulation of the previous part involved both different spatial directions as well as different particles (as e.g. on the lhs of (2.15)), become in this picture cumulants involving just different “particles” (degrees of freedom), and these kinds of cumulants are therefore the quantities of interest here.

We remark that the proof of the general Theorem that we will give 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 the existence of the moments and cumulants.

First, however, we need to introduce the general definition of multivariate cumulants,^(23,24) needed in the Theorem and its proof, and some of their properties.

3.1. Preliminaries: The General Definition and Properties of Cumulants

Here we will give the general definition of cumulants which applies to any number of variables, i.e., of the *multivariate* cumulants.^(23,24) Thereto we introduce a set of (general) random variables A_q with $q = 1 \dots Q$, for which we assume that a probability distribution function exists. The cumulant generating function of the A_q is defined as

$$\Phi(k_1, \dots, k_Q) \equiv \log \left\langle \exp \sum_{q=1}^Q i k_q A_q \right\rangle. \tag{3.7}$$

Here $\langle \rangle$ denotes an average with the probability distribution function of the A_q . Note that if the A_q are expressed in terms of yet other random variables (later, in the Theorem, the $r^{\mathcal{N}}$ and $v^{\mathcal{N}}$) the average may equivalently be taken with their probability distribution function. With the help of this generating function, the cumulants can be expressed similarly as in (2.9) by

$$\langle\langle A_1^{[n_1]}, \dots, A_Q^{[n_Q]} \rangle\rangle \equiv \left(\prod_{q=1}^Q \frac{\partial^{n_q}}{\partial (i k_q)^{n_q}} \right) \Phi(k_1, \dots, k_Q) \Big|_{\{k_q\}=0}. \tag{3.8}$$

Note that $\{k_q\} = 0$ is a short-hand notation for $k_1 = 0, k_2 = 0, \dots, k_Q = 0$. Furthermore, when one of the n_q is equal to 1, we will omit the corresponding superscript [1], e.g., $\langle\langle A_1; A_2 \rangle\rangle = \langle\langle A_1^{[1]}; A_2^{[1]} \rangle\rangle$. We stress once more that our notation is different from Van Kampen’s,⁽²⁴⁾ who writes $\langle\langle A_1^{n_1} A_2^{n_2} \dots A_Q^{n_Q} \rangle\rangle$. In particular, the square brackets in the superscripts are intended to show that they are not powers of the A_q , while the semi-colons in the expressions inside the double

angular brackets indicate that one should not interpret them as products, but as defined by (3.8). Note also that the expression $A_q^{[n_q]}$ only has a meaning inside a cumulant.

The cumulants can be expressed in terms of moments analogously to (2.11):

$$\begin{aligned} \langle\langle A_1^{[n_1]}; \dots; A_Q^{[n_Q]} \rangle\rangle &= -n_1! \cdots n_Q! \sum_{\substack{\{p_{\ell}\} \geq 0 \\ \sum_{\ell} \ell_q p_{\ell} = n_q}} \left(\sum_{\{\ell\}} p_{\ell} - 1 \right)! \prod_{\{\ell\}} \frac{1}{p_{\ell}!} \\ &\quad \times \left(- \frac{\langle A_1^{\ell_1} \dots A_Q^{\ell_Q} \rangle}{\ell_1! \cdots \ell_Q!} \right)^{p_{\ell}}, \end{aligned} \quad (3.9)$$

where $\{\ell\} = \{\ell_1, \dots, \ell_Q\}$ denotes a set of Q nonnegative ℓ_q values, $q = 1 \dots Q$ and $p_{\{\ell\}}$ gives the frequency of occurrence of that set. In (3.9) the sum is over the frequencies $p_{\{\ell\}}$ of all possible sets $\{\ell\}$ (and thus all possible moments $\langle A_1^{\ell_1} \dots A_Q^{\ell_Q} \rangle$) for which $\sum_{\ell=1}^{\infty} \ell_q p_{\ell} = n_q$. This is nothing else than factorizing the expression $A_1^{n_1} \dots A_Q^{n_Q}$ in all possible ways. Hence, the cumulants $\langle\langle A_1^{[n_1]}; \dots; A_Q^{[n_Q]} \rangle\rangle = \langle A_1^{n_1} \dots A_Q^{n_Q} \rangle \pm$ factored terms that are products of the moments $\langle A_1^{\ell_1} \dots A_Q^{\ell_Q} \rangle$ such that the ℓ_q values for fixed q add up (taking into account their frequencies $p_{\{\ell\}}$) to n_q . For some examples of multivariate cumulants, see (2.12)–(2.14).

We furthermore define the *order* n of a cumulant as the sum $n = \sum_{q=1}^Q n_q$. Note that the maximum number of moments that are multiplied in any term in (3.9) is (taking into account the frequencies) equal to the order of the cumulant.

We will now give four properties of the cumulants that follow from its definition in (3.7) and (3.8) and that can be used to manipulate expressions inside the double angular brackets of the cumulants.

(a) The first property is that, as with averages, constants may be taken in front of cumulants:

$$\langle\langle (CA_1)^{[n_1]}; \dots \rangle\rangle = C^{n_1} \langle\langle A_1^{[n_1]}; \dots \rangle\rangle \quad (3.10)$$

(b) The second property concerns cumulants where the same quantity occurs more than once:

$$\langle\langle A_1^{[n_1]}; A_1^{[n_2]}; \dots \rangle\rangle = \langle\langle A_1^{[n_1+n_2]}; \dots \rangle\rangle \quad (3.11)$$

(c) The third is a multinomial expansion:

$$\begin{aligned} \langle\langle (A_1 + \dots + A_Q)^{[n]}; \dots \rangle\rangle &= \sum_{\substack{\{k_q\} \geq 0 \\ \sum_{q=1}^Q k_q = n}} \frac{n!}{\prod_{q=1}^Q k_q!} \langle\langle A_1^{[k_1]}; \dots; A_Q^{[k_Q]}; \dots \rangle\rangle. \end{aligned} \quad (3.12)$$

(d) Finally, cumulants have the property that they are shift invariant if their orders are larger than one.^(23,24) E.g., if C_1 is a constant,

$$\langle\langle (A_1 + C_1)^{[n]}; \dots \rangle\rangle = \langle\langle A_1^{[n]}; \dots \rangle\rangle \quad (3.13)$$

Only if the order of the cumulant is one, does a shift have any effect:

$$\langle\langle A_1 + C_1 \rangle\rangle = \langle\langle A_1 \rangle\rangle + C_1. \quad (3.14)$$

3.2. The Theorem

Theorem. For a classical dynamical system of \mathcal{N} degrees of freedom described by (generalized) coordinates r_i and velocities v_i ($i = 1 \dots \mathcal{N}$), collectively denoted by $r^{\mathcal{N}}$ and $v^{\mathcal{N}}$ respectively, for which

- a) the time evolution is given by the equations of motion

$$\dot{r}_i = v_i \quad (3.15)$$

$$\dot{v}_i = a_i(r^{\mathcal{N}}, t) \quad (3.16)$$

with velocity-independent, smooth accelerations a_i , and

- b) the *initial* ensemble is described by a probability distribution in which the velocities are multivariate Gaussian⁽²⁴⁾ and independent of the coordinates r_i , i.e., with a distribution function of the form

$$\begin{aligned} \mathcal{P}(r^{\mathcal{N}}, v^{\mathcal{N}}) &= f(r^{\mathcal{N}}) \sqrt{\det [\Xi / (2\pi)]} \\ &\times \exp \left[-\frac{1}{2} \sum_{i,j=1}^{\mathcal{N}} \Xi_{ij} (v_i - u_i)(v_j - u_j) \right], \end{aligned} \quad (3.17)$$

where Ξ is a positive, symmetric $\mathcal{N} \times \mathcal{N}$ matrix with constant elements Ξ_{ij} , u_i is the average velocity corresponding to the i th degree of freedom, and $f(r^{\mathcal{N}})$ is the probability distribution of the coordinates.

When these conditions are satisfied, the cumulants⁸

$$\kappa_{\{n_i\}} \equiv \langle\langle \Delta r_1^{[n_1]}; \Delta r_2^{[n_2]}; \dots; \Delta r_{\mathcal{N}}^{[n_{\mathcal{N}}]} \rangle\rangle \quad (3.18)$$

of the displacements

$$\Delta r_i \equiv r_i(t) - r_i(0) \quad (3.19)$$

⁸ These cumulants are defined in Sec. 3.1 with $Q \rightarrow \mathcal{N}$, $q \rightarrow i$ and $A_q \rightarrow \Delta r_i$.

(whose t dependence has been suppressed) satisfy for sufficiently short initial times t

$$\kappa_{\{n_i\}} = \begin{cases} c_{\{n_i\}} t^n + \mathcal{O}(t^{n+1}) & \text{if } n \leq 2 \\ c_{\{n_i\}} t^{2n} + \mathcal{O}(t^{2n+1}) & \text{if } n > 2, \end{cases} \quad (3.20)$$

where n is the order of the cumulant given by

$$n = n_1 + n_2 + \dots + n_N. \quad (3.21)$$

The coefficients $c_{\{n_i\}}$ will be given later in (3.44) in section (3.4).

3.3. Proof of the Theorem

3.3.1. Strategy Based on Gaussian Velocities

The Theorem formulated in Eqs. (3.15–3.21) in Sec. 3.2 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 of the procedure.

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

$$\Delta r_i = \sum_{\gamma=1}^{\infty} \frac{d^\gamma r_i}{dt^\gamma} \Big|_{t=0} \frac{t^\gamma}{\gamma!} = \sum_{\gamma=1}^{\infty} \frac{d^{\gamma-1} v_i}{dt^{\gamma-1}} \Big|_{t=0} \frac{t^\gamma}{\gamma!} \quad (3.22)$$

where we used (3.15). Because of the equations of motion (3.15) and (3.16), the $d^\gamma v_i/dt^\gamma$, viewed as functions of $r^{\mathcal{N}}$ and $v^{\mathcal{N}}$ (at time t) as well as explicitly of t , are recursively related by

$$\frac{d^{\gamma+1} v_i}{dt^{\gamma+1}} = \sum_{j=1}^{\mathcal{N}} \left[v_j \frac{\partial}{\partial r_j} \left(\frac{d^\gamma v_i}{dt^\gamma} \right) + a_j(r^{\mathcal{N}}, t) \frac{\partial}{\partial v_j} \left(\frac{d^\gamma v_i}{dt^\gamma} \right) \right] + \frac{\partial}{\partial t} \left(\frac{d^\gamma v_i}{dt^\gamma} \right). \quad (3.23)$$

To show that the cumulant $\kappa_{\{n_i\}} = \mathcal{O}(t^{2n})$ for $n > 2$, it is of course possible to work out this cumulant straightforwardly using (3.9), (3.22), (3.23) and (3.17), in that order. Such a procedure was essentially followed by Schofield⁽²⁾ for $\kappa_n = \kappa_{\{n,0,0,\dots\}} = \langle \langle \Delta r_1^{[n]} \rangle \rangle$ for $n \leq 6$ and Sears⁽⁷⁾ for $n \leq 8$ 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 (3.17), 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

$\kappa_3, \kappa_4, \kappa_5$ and κ_6 naturally led us to propose the Theorem. Because the straightforward calculations 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 $\kappa_{\{n_i\}}$ for general n_i , because with increasing order $n = \sum_{i=1}^{\mathcal{N}} n_i$ 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 n th order cumulants $\kappa_{\{n_i\}} = \mathcal{O}(t^{2n})$ 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 on the velocities. This dependence has so far only been given implicitly—the cumulants are related to the moments by (3.9), the moments contain $[\Delta r_i]^\ell$, Δr_i is expanded in the time t in (3.22), and the coefficients in that expansion are the derivatives of the velocity v_i , which can be found by using (3.23) recursively. To make this more explicit, the first step of the proof will be to expand the cumulants as a powers series in the time t and the second step will be to express this series more explicitly in the velocities. In the third and last step we will then use the properties of Gaussian distributed variables, i.e., the velocities, to complete the proof of the Theorem.

It turns out that the properties of Gaussian distributed variables that we will require in the third step of the proof are formulated for *independent* Gaussian variables whose *mean is zero*, while in (3.17) the velocities are Gaussian but do not have zero mean, nor are they independent (because $\Xi_{ij} \neq 0$ for $i \neq j$ in general). For this reason, it is convenient to introduce already at this point new velocity variables whose mean is zero (cf. (3.17)):

$$V_i \equiv v_i - \langle v_i \rangle = v_i - u_i. \quad (3.24)$$

The V_i are generalizations of the peculiar velocities used in kinetic theory and will be referred to in the general case treated in this paper as *peculiar velocities* as well. For the same reason, it is convenient to get rid of the statistical dependence of the initial velocities in (3.17) by bringing the (positive) matrix Ξ to its diagonal form $\xi_i \delta_{ij}$. This can be accomplished by an orthogonal transformation. We will assume here that this orthogonal transformation has been performed so that Ξ is diagonal, and will show at the end of the proof that the form (3.20) of the Theorem is invariant under such a transformation (while the coefficients $c_{\{n_i\}}$ do change).

Substituting (3.24) into the time expansion in (3.22) and into the probability distribution (3.17) (using that Ξ is now diagonal), gives the expansion of Δr_i and the probability distribution $\mathcal{P}(r^{\mathcal{N}}, V^{\mathcal{N}})$ in their peculiar velocity form:

$$\Delta r_i = u_i t + \sum_{\gamma=1}^{\infty} \frac{t^\gamma}{\gamma!} \left. \frac{d^{\gamma-1} V_i}{dt^{\gamma-1}} \right|_{t=0}. \quad (3.25)$$

$$\mathcal{P}(r^{\mathcal{N}}, V^{\mathcal{N}}) = f(r^{\mathcal{N}}) \prod_{i=1}^{\mathcal{N}} \sqrt{2\pi\xi_i} \exp\left[-\frac{1}{2}\xi_i V_i^2\right] \quad (3.26)$$

respectively. In order to make future expressions less complicated we introduce for the coefficients in (3.25) the notation ($\gamma = 1, 2, \dots$)

$$X_{i\gamma}(r^{\mathcal{N}}, V^{\mathcal{N}}) = \frac{1}{\gamma!} \frac{d^{\gamma-1} V_i}{dt^{\gamma-1}} \Big|_{t=0}. \quad (3.27)$$

Thus (3.25) becomes

$$\Delta r_i = u_i t + \sum_{\gamma=1}^{\infty} X_{i\gamma}(r^{\mathcal{N}}, V^{\mathcal{N}}) t^{\gamma}, \quad (3.28)$$

We remark here that in the double indices of $X_{i\gamma}(r^{\mathcal{N}}, V^{\mathcal{N}})$, the first index always pertains to a particle number and will be denoted by the roman letter i , while the second pertains to an order in t and will be denoted by the Greek letter γ . Below, we will drop the explicit dependence of the $X_{i\gamma}$ on $r^{\mathcal{N}}$ and $V^{\mathcal{N}}$.

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

3.3.2. First Step: Expanding the Cumulants in the Time t

The infinite number of terms in the time expansion Δr_i in (3.28) means that to get the power expansion in t of the cumulants $\kappa_{\{n_i\}} = \langle\langle \Delta r_1^{[n_1]}, \dots, \Delta r_{\mathcal{N}}^{[n_{\mathcal{N}}]} \rangle\rangle$ occurring on the lhs of (3.20), we would use (3.9) with

$$Q \rightarrow \mathcal{N}, \quad q \rightarrow i, \quad A_q \rightarrow \Delta r_i. \quad (3.29)$$

and combine the infinite number of terms coming from (3.28). Obviously if we are interested in the cumulants up to $\mathcal{O}(t^{2n-1})$, where $n = \sum_{i=1}^{\mathcal{N}} n_i$ (cf. (3.21)), we should not have to retain all these terms in (3.28), 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 (3.28), as the following reasoning shows. The cumulants occurring on the lhs of (3.20) are given in terms of the moments $\langle \Delta r_1^{\ell_1} \Delta r_2^{\ell_2} \dots \Delta r_{\mathcal{N}}^{\ell_{\mathcal{N}}} \rangle = \langle \prod_{i=1}^{\mathcal{N}} \Delta r_i^{\ell_i} \rangle$ by (3.9). Taking the terms up to the n -th order in t in (3.28), i.e., writing $\Delta r_i = u_i t + \sum_{\gamma=1}^n X_{i\gamma} t^{\gamma} + \mathcal{O}(t^{n+1})$, it is straightforward to show that the moments satisfy

$$\left\langle \prod_{i=1}^{\mathcal{N}} \Delta r_i^{\ell_i} \right\rangle = \left\langle \prod_{i=1}^{\mathcal{N}} \left(u_i t + \sum_{\gamma=1}^n X_{i\gamma} t^{\gamma} \right)^{\ell_i} \right\rangle + \mathcal{O}(t^{n+\sum_{i=1}^{\mathcal{N}} \ell_i}) \quad (3.30)$$

so that, for given $p_{\{\ell\}}$,

$$\prod_{\{\ell\}} \left\langle \prod_{i=1}^{\mathcal{N}} \Delta r_i^{\ell_i} \right\rangle^{p_{\{\ell\}}} = \prod_{\{\ell\}} \left\langle \prod_{i=1}^{\mathcal{N}} \left(u_i t + \sum_{\gamma=1}^n X_{i\gamma} t^\gamma \right)^{\ell_i} \right\rangle^{p_{\{\ell\}}} + \mathcal{O}(t^{n+\sum_{\{\ell\}} p_{\{\ell\}} \sum_{i=1}^{\mathcal{N}} \ell_i}). \quad (3.31)$$

Products of this kind occur in the definition of the cumulants on the rhs of (3.9), and are summed over $p_{\{\ell\}}$ with the restriction that (with $q = i$ here) $\sum_{\{\ell\}} \ell_i p_{\{\ell\}} = n_i$. Since also $\sum_{i=1}^{\mathcal{N}} n_i = n$, (3.31) becomes

$$\prod_{\{\ell\}} \left\langle \prod_{i=1}^{\mathcal{N}} \Delta r_i^{\ell_i} \right\rangle^{p_{\{\ell\}}} = \prod_{\{\ell\}} \left\langle \prod_{i=1}^{\mathcal{N}} \left(u_i t + \sum_{\gamma=1}^n X_{i\gamma} t^\gamma \right)^{\ell_i} \right\rangle^{p_{\{\ell\}}} + \mathcal{O}(t^{2n}). \quad (3.32)$$

As this holds for each such expression on the rhs of 3.9 (with 3.29), we have for its lhs

$$\begin{aligned} \kappa_{\{n_i\}} &= \langle \langle \Delta r_1^{[n_1]}, \dots; \Delta r_{\mathcal{N}}^{[n_{\mathcal{N}}]} \rangle \rangle \\ &= \left\langle \left\langle \left(u_1 t + \sum_{\gamma=1}^n X_{1\gamma} t^\gamma \right)^{[n_1]} ; \dots ; \left(u_{\mathcal{N}} t + \sum_{\gamma=1}^n X_{\mathcal{N}\gamma} t^\gamma \right)^{[n_{\mathcal{N}}]} \right\rangle \right\rangle \\ &\quad + \mathcal{O}(t^{2n}). \end{aligned} \quad (3.33)$$

We remark that the first term on the 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 powers of t higher than $2n$, which we are not interested in. The second term, i.e., $\mathcal{O}(t^{2n})$ only contains powers of t of $2n$ and higher. So with (3.33) we have established that for the lower powers of t only n terms in the time expansion of Δr_i are needed, but we have not separated the powers of t lower and higher than $2n$ completely yet.

For that purpose we continue from (3.33) and use first the shift invariance property of cumulants explained at the end of Sec. 3.1, to obtain from (3.33)

$$\begin{aligned} \kappa_{\{n_i\}} &= \left\langle \left\langle \left(\sum_{\gamma=1}^n X_{1\gamma} t^\gamma \right)^{[n_1]} ; \dots ; \left(\sum_{\gamma=1}^n X_{\mathcal{N}\gamma} t^\gamma \right)^{[n_{\mathcal{N}}]} \right\rangle \right\rangle \\ &\quad + \sum_{i=1}^{\mathcal{N}} u_i t \delta_{n_i 1} \prod_{j \neq i} \delta_{n_j 0} + \mathcal{O}(t^{2n}). \end{aligned} \quad (3.34)$$

Furthermore, using the multinomial expansion in (3.12), we can write

$$\begin{aligned} \left\langle \left(\sum_{\gamma=1}^n X_{1\gamma} t^\gamma \right)^{[n_1]} ; \dots ; \left(\sum_{\gamma=1}^n X_{N\gamma} t^\gamma \right)^{[n_N]} \right\rangle &= \sum_{\substack{\{n_{i\gamma} \geq 0\} \\ \sum_{\gamma=1}^n n_{i\gamma} = n_i}} \left[\prod_{i=1}^{\mathcal{N}} \frac{n_i!}{\prod_{\gamma=1}^n n_{i\gamma}!} \right] \\ &\times \langle \langle X_{11}^{[n_{11}]}, X_{12}^{[n_{12}]}, \dots ; X_{N\mathcal{N}}^{[n_{N\mathcal{N}}]} \rangle \rangle t^{\sum_{i=1}^{\mathcal{N}} \sum_{\gamma=1}^n n_{i\gamma} \gamma} \end{aligned} \quad (3.35)$$

Note that the summation indices $n_{i\gamma}$ arise from the multinomial expansion, where i denotes a particle index and γ runs from 1 to n . For $\kappa_{\{n_i\}}$ in (3.34), 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 lower than $2n$ need to be kept. Hence, in the exponent on the rhs of (3.35), we only need terms with $\sum_{i=1}^{\mathcal{N}} \sum_{\gamma=1}^n n_{i\gamma} \gamma < 2n$. Since also $n = \sum_{i=1}^{\mathcal{N}} \sum_{\gamma=1}^n n_{i\gamma}$, we obtain $\sum_{i=1}^{\mathcal{N}} \sum_{\gamma=1}^n n_{i\gamma} \gamma < 2 \sum_{i=1}^{\mathcal{N}} \sum_{\gamma=1}^n n_{i\gamma}$, or $\sum_{i=1}^{\mathcal{N}} n_{i1} > \sum_{i=1}^{\mathcal{N}} \sum_{\gamma=2}^n n_{i\gamma} (\gamma - 2)$. Combining this condition with (3.34) and (3.35), and using $X_{i1} = V_i$ (cf. (3.27)), we find that the expansion of an n th order cumulant in time t up to $\mathcal{O}(t^{2n-1})$ is given by

$$\begin{aligned} \kappa_{\{n_i\}} &= \sum_{\substack{\{n_{i\gamma} \geq 0\} \\ \sum_{\gamma=1}^n n_{i\gamma} = n_i \\ \sum_{i=1}^{\mathcal{N}} n_{i1} > \sum_{i=1}^{\mathcal{N}} \sum_{\gamma=2}^n n_{i\gamma} (\gamma - 2)}} \left[\prod_{i=1}^{\mathcal{N}} \frac{n_i!}{\prod_{\gamma=1}^n n_{i\gamma}!} \right] \\ &\times \langle \langle V_1^{[n_{11}]}, \dots ; V_{N\mathcal{N}}^{[n_{N\mathcal{N}}]}, X_{12}^{[n_{12}]}, \dots ; X_{N\mathcal{N}}^{[n_{N\mathcal{N}}]} \rangle \rangle t^{\sum_{i=1}^{\mathcal{N}} \sum_{\gamma=1}^n n_{i\gamma} \gamma} \\ &+ \sum_{i=1}^{\mathcal{N}} u_i t \delta_{n_i 1} \prod_{j \neq i} \delta_{n_j 0} + \mathcal{O}(t^{2n}). \end{aligned} \quad (3.36)$$

We note that in (3.36) only cumulants appear, instead of moments, and, more importantly, that powers of t lower and higher than $2n$ are easily identified, something that in the straightforward moment-based approach mentioned above only happens after a lengthy calculation.

3.3.3. Second Step: Writing Cumulants in Terms of Peculiar Velocities

The dependence of $\kappa_{\{n_i\}}$ in (3.36) on the peculiar velocities $V^{\mathcal{N}}$ follows from the dependence of the $X_{i\gamma}$ on the $V^{\mathcal{N}}$.

According to (3.27), the coefficients $X_{i\gamma}$ can be determined using

$$X_{i\gamma}(r^{\mathcal{N}}, V^{\mathcal{N}}) = \tilde{X}_{i\gamma}(r^{\mathcal{N}}, V^{\mathcal{N}}, t) \Big|_{t=0}, \quad (3.37)$$

where we have defined

$$\tilde{X}_{i\gamma}(r^{\mathcal{N}}, V^{\mathcal{N}}, t) = \frac{1}{\gamma!} \frac{d^{\gamma-1} V_i}{dt^{\gamma-1}} \quad (3.38)$$

taken at time t . Below, we will suppress the explicit dependence of $\tilde{X}_{i\gamma}$ on $r^{\mathcal{N}}$, $V^{\mathcal{N}}$ and t . The $\tilde{X}_{i\gamma}$ satisfy the recursion relation, from (3.23):

$$\frac{\tilde{X}_{i\gamma+1}}{\gamma+1} = \sum_{j=1}^{\mathcal{N}} \left[(u_j + V_j) \frac{\partial \tilde{X}_{i\gamma}}{\partial r_j} + a_j(r^{\mathcal{N}}, t) \frac{\partial \tilde{X}_{i\gamma}}{\partial V_j} \right] + \frac{\partial \tilde{X}_{i\gamma}}{\partial t}. \quad (3.39)$$

For $\gamma = 2$, (3.38), (3.24) and (3.16) show that $\tilde{X}_{i2} = (dV_i/dt)/2 = a_i(r^{\mathcal{N}}, t)/2$, which is independent of $V^{\mathcal{N}}$ and is thus a polynomial in the peculiar velocities $V^{\mathcal{N}}$ of total degree zero. Using the recursion relation (3.39) one sees that if $\tilde{X}_{i\gamma}$ is a polynomial in $V^{\mathcal{N}}$ of total degree $\gamma - 2$ then on the rhs of (3.39), the term $(u_j + V_j)\partial\tilde{X}_{i\gamma}/\partial r_j$ is a polynomial of total degree $\gamma - 1$, while $a_j\partial\tilde{X}_{i\gamma}/\partial V_j$ has a total degree of $\gamma - 3$, and $\partial\tilde{X}_{i\gamma}/\partial t$ has a total degree $\gamma - 2$. The highest total power of $V^{\mathcal{N}}$ in $\tilde{X}_{i\gamma+1}$ is thus $\gamma - 1$.

In other words, for $\gamma \geq 2$, $\tilde{X}_{i\gamma}$ is a polynomial in the peculiar velocities $V^{\mathcal{N}}$ of total degree $\gamma - 2$, with coefficients that can depend on the positions of the particles. From (3.37) we then see that also $X_{i\gamma} = \tilde{X}_{i\gamma}(t = 0)$ is a polynomial in the peculiar velocities $V^{\mathcal{N}}$ of total degree $\gamma - 2$. Therefore we can write for the dependence of $X_{i\gamma}$ on $V^{\mathcal{N}}$

$$X_{i\gamma} = \sum_{p=0}^{\gamma-2} \sum_{\sum_j p_j=p} b_{i\{p_j\}}(r^{\mathcal{N}}) V_1^{p_1} \dots V_{\mathcal{N}}^{p_{\mathcal{N}}} \quad (3.40)$$

It turns out that in the third step of the proof we will not need the precise and explicit forms of the $b_{i\{p_j\}}(r^{\mathcal{N}})$, but only that the *total degree* of the polynomial $X_{i\gamma}$ is $\gamma - 2$.

3.3.4. Third Step: Using the Gaussian Nature of Velocities

Given the polynomial nature of the $X_{i\gamma}$ as a function of $V^{\mathcal{N}}$ in (3.40), we can give the following interpretation to the second condition under the summation sign in (3.36), i.e., $\sum_{i=1}^{\mathcal{N}} n_{i1} > \sum_{i=1}^{\mathcal{N}} \sum_{\gamma=2}^n n_{i\gamma}(\gamma - 2)$. Each expression of the form $X_{i\gamma}^{[n_{i\gamma}]}$ in the cumulant $\langle\langle V_1^{[n_{11}]}, \dots; V_{\mathcal{N}}^{[n_{\mathcal{N}1}]}, X_{12}^{[n_{12}]}, \dots; X_{\mathcal{N}\mathcal{N}}^{[n_{\mathcal{N}\mathcal{N}}]} \rangle\rangle$ in (3.36) (although devoid of meaning outside of cumulant brackets) signifies that $n_{i\gamma}$ is the highest power of $X_{i\gamma}$ occurring inside the averages in the expression for the cumulant in terms of moments on the right hand side of (3.9). Because $X_{i\gamma}$ is a polynomial in $V^{\mathcal{N}}$ of total degree $(\gamma - 2)$, this highest power of $X_{i\gamma}$ is a polynomial in $V^{\mathcal{N}}$ of total degree $n_{i\gamma}(\gamma - 2)$. Then, all such expressions $X_{i\gamma}^{[n_{i\gamma}]}$ together in the cumulant

$\langle\langle V_1^{[n_{i1}]}, \dots; V_{\mathcal{N}}^{[n_{\mathcal{N}1}]}, X_{12}^{[n_{12}]}, \dots; X_{\mathcal{N}n}^{[n_{\mathcal{N}n}]} \rangle\rangle$ in (3.36) generate polynomials of at most degree $\sum_{\gamma=2}^n n_{i\gamma}(\gamma - 2)$ inside the averages in the expression for the cumulant in terms of moments on the right hand side of (3.9). On the other hand the expressions $V_i^{[n_{i1}]}$ in the cumulant $\langle\langle V_1^{[n_{i1}]}, \dots; V_{\mathcal{N}}^{[n_{\mathcal{N}1}]}, X_{12}^{[n_{12}]}, \dots; X_{\mathcal{N}n}^{[n_{\mathcal{N}n}]} \rangle\rangle$ in (3.36) together generate polynomials of at most degree $\sum_{i=1}^{\mathcal{N}} n_{i1}$. Thus, the condition $\sum_{i=1}^{\mathcal{N}} n_{i1} > \sum_{i=1}^{\mathcal{N}} \sum_{\gamma=2}^n n_{i\gamma}(\gamma - 2)$ in (3.36) indicates that the total degree in $V^{\mathcal{N}}$ generated by the V_i in the cumulant $\langle\langle V_1^{[n_{i1}]}, \dots; V_{\mathcal{N}}^{[n_{\mathcal{N}1}]}, X_{12}^{[n_{12}]}, \dots; X_{\mathcal{N}n}^{[n_{\mathcal{N}n}]} \rangle\rangle$ is larger than the total degree generated by the $X_{i\gamma}$.

The crucial point is now that the auxiliary Theorem A in the Appendix can be applied to cumulants of this form. This theorem is most conveniently expressed in terms of general random variables P_q , which were used there as well to denote general random variables, but which are now polynomial functions of the peculiar velocities $V^{\mathcal{N}}$. Theorem A states that if P_q ($q = 1 \dots Q$) are polynomials of total degree d_q in the independent, zero-mean Gaussian distributed $V^{\mathcal{N}}$, and n_q and p_i are nonnegative integers, then $\langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}]}, P_1^{[n_1]}, \dots; P_Q^{[n_Q]} \rangle\rangle = 0$ if $\sum_{i=1}^{\mathcal{N}} p_i > \sum_{q=1}^Q n_q d_q$, except when all $n_{q \geq 1} = 0$ and one $p_i = 2$, in which case it becomes just $\langle\langle V_i^{[2]} \rangle\rangle$.

In order to apply Theorem A to each term in the summation on the rhs of (3.36), we need to rewrite $\langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}]}, X_{12}^{[n_{12}]}, \dots; X_{\mathcal{N}n}^{[n_{\mathcal{N}n}]} \rangle\rangle$ as $\langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}]}, P_1^{[n_1]}, \dots; P_Q^{[n_Q]} \rangle\rangle$. This can be achieved by a mapping of single to double indices, i.e., by setting

$$Q \rightarrow \mathcal{N}(n - 1) \quad (3.41a)$$

$$\begin{aligned} (P_1, n_1, d_1) &\rightarrow (X_{12}, n_{12}, 0) & (P_n, n_n, d_n) &\rightarrow (X_{22}, n_{22}, 0) \\ (P_2, n_2, d_2) &\rightarrow (X_{13}, n_{13}, 1) & (P_{n+1}, n_{n+1}, d_{n+1}) &\rightarrow (X_{23}, n_{23}, 1) \\ (P_3, n_3, d_3) &\rightarrow (X_{14}, n_{14}, 2) & &\vdots \\ &\vdots & &\vdots \end{aligned}$$

$$(P_{n-1}, n_{n-1}, d_{n-1}) \rightarrow (X_{1n}, n_{1n}, n - 2) \quad (P_Q, n_Q, d_Q) \rightarrow (X_{\mathcal{N}n}, n_{\mathcal{N}n}, n - 2) \quad (3.41b)$$

and

$$p_i \rightarrow n_{i1} \quad (3.41c)$$

Then $\sum_{q=1}^Q n_q d_q$ is seen to be equal to $\sum_{i=1}^{\mathcal{N}} \sum_{\gamma=1}^n n_{i\gamma}(\gamma - 2) = d$. As the restriction on the summation in (3.36) shows, for all terms on the rhs of (3.36) (except the $\mathcal{O}(t^{2n})$ of course), $\sum_{i=1}^{\mathcal{N}} n_{i1}$ is larger than this d . Theorem A tells us that the cumulant occurring in each term of these terms is then zero except when $n_{i2} = n_{i3} = \dots = n_{in} = 0$ for all i and only one $n_{i1} = 2$ and $n_{j \neq i1} = 0$. This

exception means, since also $\sum_{i=1}^{\mathcal{N}} \sum_{\gamma=1}^n n_{i\gamma} = n$, that $n = n_{i1} = 2$. So the only possible nonzero term in the sum in (3.36) occurs for $n = 2$. Furthermore, for $n = 1$, the last term $\sum_{i=1}^{\mathcal{N}} u_i t \delta_{n,1} \prod_{j \neq i} \delta_{n_j,0}$ in (3.36) is also left.

Thus, using Theorem A, we have shown that each term in (3.36) is zero separately except for $n = 1$ and $n = 2$, so that

$$\kappa_{\{n_i\}} = \begin{cases} \mathcal{O}(t^n) & \text{if } n \leq 2 \\ \mathcal{O}(t^{2n}) & \text{if } n > 2 \end{cases} \quad (3.42)$$

remains on the rhs of (3.36). Given that $\kappa_{\{n_i\}}$ can be expanded as a power series in t , (3.42) coincides with the formulation (3.20) of the Theorem, if we define $c_{\{n_i\}}$ as the coefficients of the t^n and t^{2n} , respectively. This is therefore now proved (with the proviso that Theorem A is proved in the Appendix), but up to this point only for diagonal matrices Ξ in the distribution (3.17).

To obtain the same result for non-diagonal matrices Ξ in, (3.17), we apply a transformation \mathbf{S} (an orthogonal $\mathcal{N} \times \mathcal{N}$ matrix with elements S_{ij}) such that $\Xi' = \mathbf{S} \cdot \Xi \cdot \mathbf{S}^T$ is diagonal. In this transformation, $r'_i = \sum_{j=1}^{\mathcal{N}} S_{ij} r_j$, $v'_i = \sum_{j=1}^{\mathcal{N}} S_{ij} v_j$ and also $\Delta r'_i = \sum_{j=1}^{\mathcal{N}} S_{ij} \Delta r_j$. Since Ξ' is diagonal, the cumulants of the primed displacements $\Delta r'_i$ satisfy the Theorem. The cumulants of the original displacements $\Delta r_i = \sum_{j=1}^{\mathcal{N}} S_{ji} \Delta r'_j$ can be expressed in terms of the primed ones using the multinomial expansion (3.12), with the result

$$\begin{aligned} \kappa_{\{n_i\}} = & \sum_{\{n_{1j}\}} \frac{n_1!}{n_{11}! \cdots n_{1\mathcal{N}}!} \cdots \sum_{\{n_{\mathcal{N}j}\}} \frac{n_{\mathcal{N}}!}{n_{\mathcal{N}1}! \cdots n_{\mathcal{N}\mathcal{N}}!} \\ & \times \langle \langle (S_{11} \Delta r'_1)^{[n_{11}]}; \dots; (S_{\mathcal{N}1} \Delta r'_{\mathcal{N}})^{[n_{1\mathcal{N}}]}; \\ & \times (S_{12} \Delta r'_1)^{[n_{21}]}; \dots; (S_{\mathcal{N}2} \Delta r'_{\mathcal{N}})^{[n_{2\mathcal{N}}]}; \dots; (S_{\mathcal{N}\mathcal{N}} \Delta r'_{\mathcal{N}})^{[n_{\mathcal{N}\mathcal{N}}]} \rangle \rangle \end{aligned} \quad (3.43)$$

Since in each term on the right hand side the $\sum_{i,j=1}^{\mathcal{N}} n_{ij} = \sum_{i=1}^{\mathcal{N}} n_i = n$ (cf. (3.12)), and each term contains the cumulants of primed displacements, which were already shown to satisfy the Theorem, each term scales as t^{2n} if $n > 2$ and as t^n if $n \leq 2$, and therefore so does the sum. This proves that (3.20) of the Theorem holds for arbitrary (positive symmetric) matrices Ξ . \square

3.4. Expression for the Coefficients in the Theorem

We will now show how one can determine the coefficients of the t^{2n} term of $\kappa_{\{n_i\}}$, i.e. $c_{\{n_i\}}$ in (3.20).

For $n = 1$ and $n = 2$, it is straightforward to show that⁽²⁴⁾

$$c_{\{1,0,0,0,\dots\}} = \langle v_1 \rangle = u_1 \quad (3.44a)$$

$$c_{\{2,0,0,0,\dots\}} = \langle V_1^2 \rangle = [\Xi^{-1}]_{11} \quad (3.44b)$$

$$c_{\{1,1,0,0,\dots\}} = \langle V_1 V_2 \rangle = [\Xi^{-1}]_{12}. \quad (3.44c)$$

(and similarly for $c_{\{0,1,0,0,0,\dots\}}$ and $c_{\{0,2,0,0,0,\dots\}}$, $c_{\{1,0,1,0,0,\dots\}}$, $c_{\{0,1,1,0,0,\dots\}}$, etc.).

To find $c_{\{n_i\}}$ for $n > 2$ one can use a similar calculation of $\kappa_{\{n_i\}}$ as used above, but taking one additional term $X_{in+1}t^{n+1}$ in the time expansion of Δr_i in (3.33) into account. Performing then the same kind of manipulations as in the proof above, one arrives for $n > 2$ at

$$c_{\{n_i\}} = \sum_{\{n_{i\gamma} \geq 0\}} \left[\frac{n_i!}{\prod_{\gamma=1}^{n+1} n_{i\gamma}!} \right] \sum_{\sum_{\gamma=1}^{n+1} n_{i\gamma} = n_i} \sum_{i=1}^{\mathcal{N}} \sum_{\gamma=1}^{n+1} \gamma n_{i\gamma} = 2n \times \langle \langle X_{11}^{[n_{11}]}, \dots; X_{1,n+1}^{[n_{1,n+1}]}, X_{21}^{[n_{21}]}, \dots; X_{\mathcal{N},n+1}^{[n_{\mathcal{N},n+1}]} \rangle \rangle. \quad (3.44d)$$

where n was defined in Eq. (3.21).

Note that for the case of a cumulant of one displacement, e.g., $\langle \langle \Delta r_i^n \rangle \rangle$ in (2.17), one has

$$c_n = c_{\{\dots,0,n,0,\dots\}} \quad (3.45)$$

where the n on the rhs is at the i th position.

Using (3.44d), we can give some examples of c_n for $n = 3$ and $n = 4$:

$$c_3 = 3 \langle \langle V_i^{[2]}; X_{i4} \rangle \rangle + 6 \langle \langle V_i; X_{i2}; X_{i3} \rangle \rangle + \langle \langle X_{i2}^{[3]} \rangle \rangle \quad (3.46)$$

$$c_4 = 4 \langle \langle V_i^{[3]}; X_{i5} \rangle \rangle + 6 \langle \langle V_i^{[2]}; X_{i3}^{[2]} \rangle \rangle + 12 \langle \langle V_i^{[2]}; X_{i2}; X_{i4} \rangle \rangle + 12 \langle \langle V_i; X_{i2}^{[2]}; X_{i3} \rangle \rangle + \langle \langle X_{i2}^{[4]} \rangle \rangle. \quad (3.47)$$

while an example of the coefficients $c_{\{n_i\}}$ for cumulants involving different degrees of freedom, e.g. $\langle \langle \Delta r_1; \Delta r_2; \Delta r_3 \rangle \rangle$ is, from (3.44d),

$$c_{\{1,1,1,0,0,\dots\}} = \langle \langle V_1; V_2; X_{34} \rangle \rangle + \langle \langle V_1; X_{22}; X_{33} \rangle \rangle + \langle \langle V_1; X_{23}; X_{32} \rangle \rangle + \langle \langle V_1; X_{24}; X_{31} \rangle \rangle + \langle \langle X_{12}; V_2; X_{33} \rangle \rangle + \langle \langle X_{12}; X_{22}; X_{32} \rangle \rangle + \langle \langle X_{12}; X_{23}; V_3 \rangle \rangle + \langle \langle X_{13}; V_2; X_{32} \rangle \rangle + \langle \langle X_{13}; X_{22}; V_3 \rangle \rangle + \langle \langle X_{14}; V_2; V_3 \rangle \rangle. \quad (3.48)$$

We note that although the $X_{i\gamma}$ are useful to derive these expressions for $c_{\{n_i\}}$, to evaluate them in practice requires additional work. One would first need to write the $X_{i\gamma}$ as $\tilde{X}_{i\gamma}(r^{\mathcal{N}}, V^{\mathcal{N}}, t = 0)$ using (3.37), and work out the recursion relation (3.39). Furthermore, the cumulants would have to be written in terms of averages using (3.9). The values of these averages will depend on the system, i.e., the accelerations a_i , and their evaluation will in general require a numerical approach, which we will explore in future work.

4. CONCLUSIONS

In this paper, we have proved a mathematical theorem on the correlations of the initial time displacements of particles (or in general of coordinates associated with degrees of freedom) for a class of dynamical systems whose main restriction is that the initial distribution of the velocity-variables is a (multivariate) Gaussian, independent of the position-variables.

Among the physical applications of this Theorem is the result that a well-known short-time expansion of the Van Hove self-correlation is well-behaved: each subsequent term in the expansion is smaller than the previous one for small enough t , something which had been suspected but not established before. It has also been shown on the basis of the Theorem that in the studies of undercooled liquids and glasses, using cumulants instead of the usual non-Gaussian parameters may give more physical information. Furthermore, it was shown that the expansion used in the Green's functions theory is also well-behaved if the velocity distributions are initially Gaussian, so that this theory, which can describe non-equilibrium mass transport processes on short time and length scales, has now been given a firmer basis.

APPENDIX

In the third step of the proof of the main Theorem, we needed the following auxiliary theorem to prove the main Theorem.

Theorem A. *Let V_i be a set of \mathcal{N} statistically independent, zero-mean Gaussian variables, collectively denoted by $V^{\mathcal{N}}$, and let P_q ($q = 1 \dots Q$) be a set of Q polynomials in $V^{\mathcal{N}}$ of total degree d_q . Let p_i ($i = 1 \dots \mathcal{N}$) and n_q ($q = 1 \dots Q$) be nonnegative integer numbers. Then if*

$$\sum_{i=1}^{\mathcal{N}} p_i > \sum_{q=1}^Q n_q d_q \quad (\text{A.1})$$

and at least one $n_q \neq 0$, the following cumulant vanishes:

$$\langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}]}, P_1^{[n_1]}, \dots; P_Q^{[n_Q]}\rangle\rangle = 0 \quad (\text{A.2})$$

while if all n_q are zero, one has

$$\langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}]}\rangle\rangle = \sum_{i=1}^{\mathcal{N}} \langle\langle V_i^{[2]}\rangle\rangle \delta_{p_i, 2} \prod_{j \neq i} \delta_{p_j, 0}. \quad (\text{A.3})$$

Proof of Theorem A. 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 $\theta^{\mathcal{N}}$ -modified average. This definition will serve, in conjunction with Lemma 1 below, to construct a convenient generating function (which takes the form of a $\theta^{\mathcal{N}}$ -modified cumulant) for the quantities $\langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}]}, P_1^{[n_1]}, \dots; P_Q^{[n_Q]}\rangle\rangle$ that occur in Theorem A. Working with this generating function will be more convenient than trying to calculate each $\langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}]}, P_1^{[n_1]}, \dots; P_Q^{[n_Q]}\rangle\rangle$ individually. After this generating function has been introduced, Lemma 2 and Lemma 3 are presented and proved, which use the Gaussian nature of the V_i to give properties of averages and $\theta^{\mathcal{N}}$ -modified averages of powers of the V_i , which allow one to prove a polynomial property (Lemma 4) of the generating function of the quantities $\langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}]}, P_1^{[n_1]}, \dots; P_Q^{[n_Q]}\rangle\rangle$. This polynomial property will be the central ingredient to complete the proof.

First we remark that below, $V^{\mathcal{N}}$ will always denote the same set of \mathcal{N} statistically independent, zero-mean Gaussian distributed variables V_i of Theorem A.

The definition of $\theta^{\mathcal{N}}$ -modified averages and cumulants is:

Definition. The $\theta^{\mathcal{N}}$ -modified average of a general variable P (which below will always be a polynomial in $V^{\mathcal{N}}$) is defined as

$$\langle P \rangle_{\theta^{\mathcal{N}}} \equiv \frac{\langle P \exp \sum_{i=1}^{\mathcal{N}} \theta_i V_i \rangle}{\langle \exp \sum_{i=1}^{\mathcal{N}} \theta_i V_i \rangle} = e^{-\frac{1}{2} \sum_{i=1}^{\mathcal{N}} \theta_i^2 \langle V_i^2 \rangle} \left\langle P \exp \sum_{i=1}^{\mathcal{N}} \theta_i V_i \right\rangle \quad (\text{A.4})$$

where the θ_i ($i = 1 \dots \mathcal{N}$) are real numbers.

Similarly, $\theta^{\mathcal{N}}$ -modified moments are generally defined as the $\theta^{\mathcal{N}}$ -modified averages of powers of general variables (i.e., functions of $V^{\mathcal{N}}$, and in the main text also of $r^{\mathcal{N}}$), and $\theta^{\mathcal{N}}$ -modified cumulants are defined as having the same relation to $\theta^{\mathcal{N}}$ -modified moments as normal cumulants have to normal moments. $\theta^{\mathcal{N}}$ -modified cumulants are therefore also given through the $\theta^{\mathcal{N}}$ -modified cumulant

generating function as:

$$\langle\langle P_1^{[n_1]}, \dots; P_Q^{[n_Q]} \rangle\rangle_{\theta^{\mathcal{N}}} \equiv \prod_{q=1}^Q \frac{\partial^{n_q}}{\partial (ik_q)^{n_q}} \log \left\langle \exp \sum_{q=1}^Q ik_q P_q \right\rangle_{\theta^{\mathcal{N}}} \Big|_{\{k_q\}=0}. \quad (\text{A.5})$$

The generating function nature of the $\theta^{\mathcal{N}}$ -modified cumulants follows from:

Lemma 1. (relation between cumulants and $\theta^{\mathcal{N}}$ -modified cumulants)⁹ *The $\theta^{\mathcal{N}}$ -modified cumulants of a set of variables P_1, \dots, P_Q are related to the normal cumulants by*

$$\begin{aligned} \langle\langle P_1^{[n_1]}, \dots; P_Q^{[n_Q]} \rangle\rangle_{\theta^{\mathcal{N}}} &= \sum_{p_1=0}^{\infty} \dots \sum_{p_{\mathcal{N}}=0}^{\infty} \left[\prod_{i=1}^{\mathcal{N}} \frac{\theta_i^{p_i}}{p_i!} \right] \\ &\times \langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}}]}; P_1^{[n_1]}, \dots; P_Q^{[n_Q]} \rangle\rangle \end{aligned} \quad (\text{A.6})$$

if at least one $n_q \neq 0$, while it is zero otherwise.

Proof. For case in which at least one n_q is nonzero, we start with the rhs of (A.6) and use the expression for the cumulants in (3.8):

$$\begin{aligned} &\sum_{p_1=0}^{\infty} \dots \sum_{p_{\mathcal{N}}=0}^{\infty} \left[\prod_{i=1}^{\mathcal{N}} \frac{\theta_i^{p_i}}{p_i!} \right] \langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}}]}; P_1^{[n_1]}, \dots; P_Q^{[n_Q]} \rangle\rangle \\ &= \sum_{p_1=0}^{\infty} \dots \sum_{p_{\mathcal{N}}=0}^{\infty} \prod_{i=1}^{\mathcal{N}} \frac{\theta_i^{p_i}}{p_i!} \frac{\partial^{p_i}}{\partial (ik'_i)^{p_i}} \prod_{q=1}^Q \frac{\partial^{n_q}}{\partial (ik_q)^{n_q}} \\ &\times \log \left\langle \exp \left[\sum_{i=1}^{\mathcal{N}} ik'_i V_i + \sum_{q=1}^Q ik_q P_q \right] \right\rangle_{\{k_q\}=\{k'_i\}=0} \end{aligned} \quad (\text{A.7})$$

We recognize the Taylor series, i.e., that $\sum_{p_i=0}^{\infty} [(-i\theta_i)^{p_i} / p_i!] \partial^{p_i} f(k'_i) / \partial k'_i{}^{p_i} \Big|_{k'_i=0} = f(-i\theta_i)$ to write this as

$$\begin{aligned} &\sum_{p_1=0}^{\infty} \dots \sum_{p_{\mathcal{N}}=0}^{\infty} \left[\prod_{i=1}^{\mathcal{N}} \frac{\theta_i^{p_i}}{p_i!} \right] \langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}}]}; P_1^{[n_1]}, \dots; P_Q^{[n_Q]} \rangle\rangle \\ &= \prod_{q=1}^Q \frac{\partial^{n_q}}{\partial (ik_q)^{n_q}} \log \left\langle \exp \left[\sum_{i=1}^{\mathcal{N}} \theta_i V_i + \sum_{q=1}^Q ik_q P_q \right] \right\rangle_{\{k_q\}=0} \end{aligned} \quad (\text{A.8})$$

⁹ For $\mathcal{N} = Q = n_1 = 1$ this lemma coincides with the last exercise of section XVI.3 in Van Kampen's book.⁽²⁴⁾

Using definition (A.4), we obtain

$$\begin{aligned} & \sum_{p_1=0}^{\infty} \cdots \sum_{p_{\mathcal{N}}=0}^{\infty} \left[\prod_{i=1}^{\mathcal{N}} \frac{\theta_i^{p_i}}{p_i!} \right] \langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}]}, P_1^{[n_1]}, \dots; P_Q^{[n_Q]}] \rangle\rangle \\ &= \prod_{q=1}^Q \frac{\partial^{n_q}}{\partial (ik_q)^{n_q}} \left[\log \left\langle \exp \sum_{q=1}^Q ik_q P_q \right\rangle_{\theta^{\mathcal{N}}} + \frac{1}{2} \sum_{i=1}^{\mathcal{N}} \theta_i^2 \langle V_i^2 \rangle \right] \Big|_{\{k_q\}=0} \quad (\text{A.9}) \end{aligned}$$

Since we are considering the case that at least one n_q is nonzero, the contribution from the k_q -independent $\frac{1}{2} \sum_{i=1}^{\mathcal{N}} \theta_i^2 \langle V_i^2 \rangle$ vanishes when $\partial/\partial(ik_q)$ acts on it. The remainder on the rhs of (A.9) is by definition (A.5) equal to the lhs of (A.6).

The case $n_1 = \dots = n_Q = 0$ is trivial, for then $\langle\langle P_1^{n_1} \dots P_Q^{n_Q} \rangle\rangle_{\theta^{\mathcal{N}}} = 0$ since a zeroth cumulant is always zero. \square

A consequence of this lemma, i.e., of (A.6), is that repeated derivatives with respect to θ_i of $\langle\langle P_1^{[n_1]}, \dots; P_Q^{[n_Q]} \rangle\rangle_{\theta^{\mathcal{N}}}$ taken at $\theta_i = 0$ generate the $\langle\langle V_1^{[p_1]}, \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}]}, P_1^{[n_1]}, \dots; P_Q^{[n_Q]}] \rangle\rangle$.

The second lemma concerns the average of a product of powers of the V_i and a single polynomial in $V^{\mathcal{N}}$.

Lemma 2. (Averages of powers of V_i times a polynomial in $V^{\mathcal{N}}$) *Let P be a polynomial function of total degree d in $V^{\mathcal{N}}$. Given a set of \mathcal{N} nonnegative integers s_i , collectively denoted by $s^{\mathcal{N}}$, and a set of \mathcal{N} “parities” δ_i with each δ_i zero or one, one can write*

$$\left\langle \prod_{i=1}^{\mathcal{N}} V_i^{2s_i + \delta_i} P \right\rangle = P_{s^*}(\{s_j\}) \prod_{i=1}^{\mathcal{N}} (2s_i + 2\delta_i - 1)!! \langle V_i^2 \rangle^{s_i} \quad (\text{A.10})$$

where $P_{s^*}(\{s_j\})$ is a polynomial in the s_j of total degree s^* , which satisfies

$$s^* \leq \frac{d - \sum_{i=1}^{\mathcal{N}} \delta_i}{2}. \quad (\text{A.11})$$

Proof. We start by writing out the polynomial P as

$$P = \sum_{\substack{\{p_i\} \\ \sum_{i=1}^{\mathcal{N}} p_i \leq d}} b_{\{p_i\}} \prod_{i=1}^{\mathcal{N}} V_i^{p_i}. \quad (\text{A.12})$$

Of these terms, only those with the same “parity” as the δ_i (i.e., if $\delta_i = 0$, p_i is even and if $\delta_i = 1$, p_i is odd) contribute to the average $\langle \prod_{i=1}^{\mathcal{N}} V_i^{2s_i + \delta_i} P \rangle$, due to

the even nature of the distribution of the V_i . Thus, one can write $p_i = 2s'_i + \delta_i$ and obtain

$$\left\langle \prod_{i=1}^{\mathcal{N}} V_i^{2s_i + \delta_i} P \right\rangle = \sum_{\{s'_i\}} b_{\{2s'_i + \delta_i\}} \prod_{i=1}^{\mathcal{N}} \langle V_i^{2(s_i + s'_i + \delta_i)} \rangle. \quad (\text{A.13})$$

$\sum_{i=1}^{\mathcal{N}} (2s'_i + \delta_i) \leq d$

Using $\langle V_i^{2s} \rangle = (2s - 1)!! \langle V_i^2 \rangle^s$,⁽²³⁾ we obtain

$$\begin{aligned} \left\langle \prod_{i=1}^{\mathcal{N}} V_i^{2s_i + \delta_i} P \right\rangle &= \sum_{\{s'_i\}} b_{\{2s'_i + \delta_i\}} \prod_{i=1}^{\mathcal{N}} (2s_i + 2s'_i + 2\delta_i - 1)!! \langle V_i^2 \rangle^{s_i + s'_i + \delta_i} \\ &= \sum_{\{s'_i\}} b_{\{2s'_i + \delta_i\}} \prod_{i=1}^{\mathcal{N}} \frac{(2s_i + 2s'_i + 2\delta_i - 1)!!}{(2s_i + 2\delta_i - 1)!!} \langle V_i^2 \rangle^{s'_i + \delta_i} \\ &\quad \times \prod_{i=1}^{\mathcal{N}} (2s_i + 2\delta_i - 1)!! \langle V_i^2 \rangle^{s_i} \end{aligned} \quad (\text{A.14})$$

$\sum_{i=1}^{\mathcal{N}} (2s'_i + \delta_i) \leq d$

This is of the form stated in (A.10), where

$$P_{s^*}(\{s_j\}) = \sum_{\{s'_i\}} b_{\{2s'_i + \delta_i\}} \prod_{i=1}^{\mathcal{N}} \prod_{s''_i=1}^{s'_i} (2s_i + 2s''_i + 2\delta_i - 1) \langle V_i^2 \rangle^{s'_i + \delta_i} \quad (\text{A.15})$$

$\sum_{i=1}^{\mathcal{N}} (2s'_i + \delta_i) \leq d$

This shows that P_{s^*} is a polynomial in $s^{\mathcal{N}}$, since it depends on the s_i only through finitely many factors $(2s_i + 2s''_i + 2\delta_i - 1)$. In fact, for each term in (A.15), the number of such factors is $\sum_{i=1}^{\mathcal{N}} s'_i$. Because of the restriction on the sum over $\{s'_i\}$ in (A.15), this number $\sum_{i=1}^{\mathcal{N}} s'_i$ is less than or equal to $(d - \sum_{i=1}^{\mathcal{N}} \delta_i)/2$ for each term. The total degree s^* of the polynomial $P_{s^*}(\{s_j\})$, which is the maximum of this number over all the terms, therefore also satisfies $s^* \leq (d - \sum_{i=1}^{\mathcal{N}} \delta_i)/2$. \square

The third lemma concerns a polynomial property of the $\theta^{\mathcal{N}}$ -modified averages of polynomials P in $V^{\mathcal{N}}$.

Lemma 3. (polynomial property of the $\theta^{\mathcal{N}}$ -modified average of a polynomial in $V^{\mathcal{N}}$) *Let P be a polynomial of total degree d in $V^{\mathcal{N}}$. Then the $\theta^{\mathcal{N}}$ -modified average of P is a polynomial in $\theta^{\mathcal{N}}$ of at most the same total degree d .*

Proof. a) Consider first the case that P is a polynomial in the V_i of total degree d and of definite “parity” for each i , i.e., that it either changes sign or remains unchanged when V_i is replaced by $-V_i$. Define the numbers δ_i such that $\delta_i = 0$ if P is even in V_i and $\delta_i = 1$ if it is odd. By the definition of the $\theta^{\mathcal{N}}$ -modified average in (A.4), expanding the exponent, and using that only even powers of V_i have a non-zero average, one gets

$$\begin{aligned} \langle P \rangle_{\theta^{\mathcal{N}}} &= e^{-\frac{1}{2} \sum_{i=1}^{\mathcal{N}} \theta_i^2 \langle V_i^2 \rangle} \\ &\times \sum_{s_1=0}^{\infty} \cdots \sum_{s_{\mathcal{N}}=0}^{\infty} \left[\prod_{i=1}^{\mathcal{N}} \frac{\theta_i^{2s_i+\delta_i}}{(2s_i+\delta_i)!} \right] \left\langle \prod_{i=1}^{\mathcal{N}} V_i^{2s_i+\delta_i} P \right\rangle \end{aligned} \quad (\text{A.16})$$

Using (A.10) of Lemma 2 and that $(2s_i-1+2\delta_i)!/(2s_i+\delta_i)! = 1/(2^{s_i}s_i!)$, we obtain

$$\begin{aligned} \langle P \rangle_{\theta^{\mathcal{N}}} &= e^{-\frac{1}{2} \sum_{i=1}^{\mathcal{N}} \theta_i^2 \langle V_i^2 \rangle} \sum_{\{s_i \geq 0\}} \prod_{i=1}^{\mathcal{N}} \frac{\theta_i^{2s_i+\delta_i} \langle V_i^2 \rangle^{s_i+\delta_i}}{2^{s_i} s_i!} P_{s^*}(\{s_j\}) \\ &= \left[\prod_{i=1}^{\mathcal{N}} [(\langle V_i^2 \rangle \theta_i)^{\delta_i}] \right] e^{-\frac{1}{2} \sum_{i=1}^{\mathcal{N}} \theta_i^2 \langle V_i^2 \rangle} \sum_{\{s_i \geq 0\}} P_{s^*}(\{s_j\}) \prod_{i=1}^{\mathcal{N}} \frac{[\frac{1}{2} \theta_i^2 \langle V_i^2 \rangle]^{s_i}}{s_i!} \end{aligned} \quad (\text{A.17})$$

Note that the polynomial P_{s^*} in s_j inside the $\{s_i\}$ summation can be generated from an expression that does not have this polynomial by applying operators $\theta_j^2(\partial/\partial\theta_j^2)$, e.g.,

$$\begin{aligned} \sum_{\{s_i \geq 0\}} s_j \prod_{i=1}^{\mathcal{N}} \frac{[\frac{1}{2} \theta_i^2 \langle V_i^2 \rangle]^{s_i}}{s_i!} &= \theta_j^2 \frac{\partial}{\partial \theta_j^2} \sum_{\{s_i \geq 0\}} \prod_{i=1}^{\mathcal{N}} \frac{[\frac{1}{2} \theta_i^2 \langle V_i^2 \rangle]^{s_i}}{s_i!}, \\ &= \theta_j^2 \frac{\partial}{\partial \theta_j^2} e^{\frac{1}{2} \sum_{i=1}^{\mathcal{N}} \theta_i^2 \langle V_i^2 \rangle}. \end{aligned} \quad (\text{A.18})$$

and in general

$$\sum_{\{s_i \geq 0\}} P_{s^*}(\{s_j\}) \prod_{i=1}^{\mathcal{N}} \frac{[\frac{1}{2} \theta_i^2 \langle V_i^2 \rangle]^{s_i}}{s_i!} = P_{s^*} \left(\left\{ \theta_j^2 \frac{d}{d\theta_j^2} \right\} \right) e^{\frac{1}{2} \sum_{i=1}^{\mathcal{N}} \theta_i^2 \langle V_i^2 \rangle}. \quad (\text{A.19})$$

Combining this with (A.17) gives

$$\langle P \rangle_{\theta^{\mathcal{N}}} = \left[\prod_{i=1}^{\mathcal{N}} [(\langle V_i^2 \rangle \theta_i)^{\delta_i}] \right] e^{-\frac{1}{2} \sum_{i=1}^{\mathcal{N}} \theta_i^2 \langle V_i^2 \rangle} P_{s^*} \left(\left\{ \theta_j^2 \frac{\partial}{\partial \theta_j^2} \right\} \right) e^{\frac{1}{2} \sum_{i=1}^{\mathcal{N}} \theta_i^2 \langle V_i^2 \rangle}. \quad (\text{A.20})$$

In this expression, the differential operators $(\partial/\partial\theta_j^2)$ “bring down” factors of θ_j^2 from the exponent to its right. That exponent itself is then canceled by the exponent to the left of the P_{s^*} operator, so that only a polynomial in $\theta^{\mathcal{N}}$ is left. The total degree of this polynomial is twice the maximum number of factors brought down by the operators (twice because the squares of the θ_j are brought down). This maximum number is simply the total degree of P_{s^*} , i.e., s^* . Counting finally also the powers of θ_i of the first product in (A.20), we see that $\langle P \rangle_{\theta^{\mathcal{N}}}$ is a polynomial in $\theta^{\mathcal{N}}$ of total degree $d' = 2s^* + \sum_{i=1}^{\mathcal{N}} \delta_i$. But Lemma 2, in particular (A.11), says that $s^* \leq (d - \sum_{i=1}^{\mathcal{N}} \delta_i)/2$, so that for a polynomial P of definite parity, its total degree d' satisfies $d' \leq d$.

b) To show that the same is true for a general polynomial, note that any polynomial P can always be written as a sum of polynomials of definite parity. Since the $\theta^{\mathcal{N}}$ -modified average of that sum is the sum of the $\theta^{\mathcal{N}}$ -modified average of each term, and each term is a polynomial in $\theta^{\mathcal{N}}$ of total degree $d' \leq d$, $\langle P \rangle_{\theta^{\mathcal{N}}}$ is also a polynomial in $\theta^{\mathcal{N}}$ of total degree $d' \leq d$. \square

The next and final lemma we need before we can prove Theorem A concerns $\theta^{\mathcal{N}}$ -modified cumulants of several polynomials in $V^{\mathcal{N}}$.

Lemma 4. ($\theta^{\mathcal{N}}$ -modified cumulants of polynomials in $V^{\mathcal{N}}$) *Let P_q ($q = 1 \dots Q$) be a set of polynomials of total degree d_q in the $V^{\mathcal{N}}$. Then the $\theta^{\mathcal{N}}$ -modified cumulant $\langle\langle P_1^{[n_1]}, \dots, P_Q^{[n_Q]} \rangle\rangle_{\theta^{\mathcal{N}}}$ is a polynomial in $\theta^{\mathcal{N}}$ of a total degree of at most $d = \sum_{q=1}^Q n_q d_q$.*

Proof. Because the $\theta^{\mathcal{N}}$ -modified cumulants are defined formally in precisely the same way as normal cumulants [i.e., (A.5) vs. (3.8)], the relation (3.9) between cumulants and moments applies to the $\theta^{\mathcal{N}}$ -modified cumulants and moments as well. According to that relation, the $\theta^{\mathcal{N}}$ -modified cumulant $\langle\langle P_1^{[n_1]}, \dots, P_Q^{[n_Q]} \rangle\rangle_{\theta^{\mathcal{N}}}$ can be expressed as a sum of terms each of which contains a product of the moments $\langle P_1^{\ell_1} \dots P_Q^{\ell_Q} \rangle_{\theta^{\mathcal{N}}}$ raised to the power $p_{\{\ell\}}$ (where the product is over all possible sets $\{\ell\} = \{\ell_1, \dots, \ell_Q\}$ with the restrictions stated in (3.9)). Because P_q is required by the conditions of the lemma to be a polynomial in $V^{\mathcal{N}}$ of total degree d_q , $P_q^{\ell_q}$ is a polynomial in $V^{\mathcal{N}}$ of total degree $\ell_q d_q$, and the product $P_1^{\ell_1} \dots P_Q^{\ell_Q}$ is a polynomial in $V^{\mathcal{N}}$ of total degree $\sum_{q=1}^Q \ell_q d_q$. According to Lemma 3, each $\theta^{\mathcal{N}}$ -modified moment $\langle P_1^{\ell_1} \dots P_Q^{\ell_Q} \rangle_{\theta^{\mathcal{N}}}$ is then a polynomial in $\theta^{\mathcal{N}}$ of a total degree of at most $\sum_{q=1}^Q \ell_q d_q$. Its $p_{\{\ell\}}$ -th power in (3.9) is then a polynomial in $\theta^{\mathcal{N}}$ of total degree $p_{\{\ell\}} \sum_{q=1}^Q \ell_q d_q$ (at most), and the product (over $\{\ell\}$) that occurs on the rhs of (3.9) is of total degree $d \equiv \sum_{\{\ell\}} p_{\{\ell\}} \sum_{q=1}^Q \ell_q d_q$ (at most). Since $p_{\{\ell\}}$ is summed over in (3.9) with the restriction that $\sum_{\{\ell\}} p_{\{\ell\}} \ell_q = n_q$, the total degree

d of the expressions $\prod_{\{\ell\}} \langle P_1^{\ell_1} \cdots P_Q^{\ell_Q} \rangle_{\theta^{\mathcal{N}}}^{p_{\{\ell\}}}$ can be rewritten as $d = \sum_{q=1}^Q n_q d_q$ (at most). Each term in the sum over $p_{\{\ell\}}$ on the rhs of (3.9) is therefore (at most) of this total degree d , so that the full expression, i.e. $\langle\langle P_1^{[n_1]}; \dots; P_Q^{[n_Q]} \rangle\rangle_{\theta^{\mathcal{N}}}$, is also a polynomial in $\theta^{\mathcal{N}}$ of a total degree of at most d . \square

Conclusion of the proof of Theorem A

We can now finish the proof of Theorem A. To consider $\langle\langle V_1^{[p_1]}; \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}}]}; P_1^{[n_1]}; \dots; P_Q^{[n_Q]} \rangle\rangle$ as on the lhs of (A.2) in the case that at least one $n_q \neq 0$, we look at its generating function, i.e., $\langle\langle P_1^{[n_1]}; \dots; P_Q^{[n_Q]} \rangle\rangle_{\theta^{\mathcal{N}}}$. According to (A.6) of Lemma 1, this generating function admits a power series in $\theta^{\mathcal{N}}$. At the same time, according to Lemma 4 (whose proof required Lemmas (2) and (3)), $\langle\langle P_1^{[n_1]}; \dots; P_Q^{[n_Q]} \rangle\rangle_{\theta^{\mathcal{N}}}$ is given by a polynomial in $\theta^{\mathcal{N}}$ of a total degree of at most $d = \sum_{q=1}^Q n_q d_q$, so its power series in $\theta^{\mathcal{N}}$ in (A.6) terminates (at the latest) after $\sum_{i=1}^{\mathcal{N}} p_i = d$. Since these lemmas should be valid for all $\theta^{\mathcal{N}}$, each coefficient of the terms with $\sum_{i=1}^{\mathcal{N}} p_i > d$ must be zero, i.e., using (A.6) of Lemma 1, $\langle\langle V_1^{[p_1]}; \dots; V_{\mathcal{N}}^{[p_{\mathcal{N}}]}; P_1^{[n_1]}; \dots; P_Q^{[n_Q]} \rangle\rangle = 0$, which is (A.2) of Theorem A. Finally, for the case $n_q = 0$ for all $q = 1 \dots Q$, (A.3) of Theorem A follows simply from the zero-mean Gaussian nature of the V_i and their statistical independence. \square

ACKNOWLEDGMENTS

The authors would like to thank Prof. H. van Beijeren and Prof. F. Bonetto for carefully reading the manuscript and for their helpful suggestions. 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.

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