PHYSICAL REVIEW E, VOLUME 65, 011106

Mode-coupling theory for multiple-point and multiple-time correlation functions

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(Received 1 August 2001; published 18 December 2001)

We present a theoretical framework for higher-order correlation functions involving multiple times and multiple points in a classical, many-body system. Such higher-order correlation functions have attracted much interest recently in the context of various forms of multidimensional spectroscopy, and have found an intriguing application as proposed measures of dynamical heterogeneities in structural glasses. The theoretical formalism is based upon projection operator techniques that are used to isolate the slow time evolution of dynamical variables by expanding the slowly evolving component of arbitrary variables in an infinite, ‘‘multilinear’’ basis composed of the products of slow variables of the system. Using the formalism, a formally exact mode coupling theory is derived for multiple-point and multiple-time correlation functions. The resulting expressions for higher-order correlation functions are made tractable by applying a rigorous perturbation scheme, called the *N*-ordering method, which is exact for systems with finite correlation lengths in the thermodynamic limit. The theory is contrasted with standard mode coupling theories in which the noise or fluctuating force appearing in the generalized Langevin equation is assumed to be Gaussian, and it is demonstrated that the non-Gaussian nature of the fluctuating forces leads to important contributions to higher-order correlation functions. Finally, the higher-order correlation functions are evaluated analytically for an ideal gas system for which it is shown that the mode coupling theory is exact.

DOI: 10.1103/PhysRevE.65.011106 PACS number(s): 05.20.Jj, 61.20.Lc, 05.40.−a

I. INTRODUCTION

In a glassy system where structural frustration prevents relaxation to equilibrium, dynamical properties often demonstrate complicated time dependence [1]. For instance, in dense colloidal systems, at a given time some regions of the complex fluid are essentially static and crystalline, while the dynamics in other regions exhibit behavior that is associated with fluids. In these systems, structural rearrangement occurs through relatively rapid, collective, stringlike motions [2,3]. Furthermore, at later times, a region of the fluid that previously appeared crystalline may exhibit fluidlike properties. Such heterogeneous behavior is characteristic for structural glasses and supercooled complex fluids [4–9]. To describe this behavior, it is natural to examine how the local density of the liquid is correlated over various spatial domains [10,11], or—when one is more interested in the different time scales of slow global changes of structure and the local decay of correlations—multiple time correlation functions [12]. Both types of higher-order correlation functions have recently been proposed and used as measures for characterizing ‘‘dynamical heterogeneities’’ in structural glasses.

A number of experimental probes for examining detailed dynamical features taking place on various length and time scales in glassy systems have emerged over the last few years. These new approaches have the potential to provide extremely useful information on how collective motions of the system are correlated to specific statistical features of the dynamics such as the distribution of time scales of fluctuations, the length scale and size distribution of solidlike clusters, and cage structural relaxation rates. One approach to probe the nature of dynamical heterogeneities is based on single-molecule spectroscopy techniques [13–16] in which the environment of a one molecule is tracked over a period of time. The technique allows the information of not only the distribution of heterogeneous environments but also the explicit reorganization times that are present in the system, since the individual measurements are not statistically averaged. A somewhat different experimental approach is based on multidimensional nuclear magnetic resonance [17,18] and nonresonant nonlinear Raman spectroscopy [19–21]. The response function in these experiments can be related to higher-order correlation functions using response theory [22,23].

Given the interest in multiple-time and multiple-point correlation functions, the need for a theory that accurately predicts these quantities is clear. Surprisingly, there has been relatively little work along these lines and the literature is not nearly as extensive as it for ordinary, two-time, two-point correlation functions such as the dynamic structure factor. Although there have been several recent microscopic theories for the off-resonant fifth-order response function for simple liquids [24,25], little work has been done on constructing microscopic theories for general higher-order correlation functions since the kinetic theories of de Schepper and Ernst [26], who attempted to extract the nonanalytic density contributions to the Burnett coefficients in hard-sphere liquids.

A common approach to describing the dynamical properties of liquids and complex fluids at long times is based on the generalized Langevin equation [27]. The basic utility of the generalized Langevin equation depends on the assumption that the long-time behavior of an arbitrary dynamical variable of the system can be written in terms of the dynamics of a specific set of slow modes. This slow behavior can be isolated by extracting the projection of the dynamical variable onto the slow modes, which effectively form a basis set for the long-time behavior of the system. This approach has been successfully applied to describe relaxation and simple time correlation functions in a wide variety of condensed phase systems. In the context of simple liquid systems, it was initially assumed that only the linear densities of conserved variables of the system composed the set of slow variables of the system [28–30]. However, it was discovered that this basis set was insufficient [31] to describe the complex, nonexponential relaxation of simple time correlation functions observed in molecular dynamics simulations [32]. The subsequent observation that theories incorporating multilinear products of the linear densities in the basis were capable of yielding the correct asymptotic long-time behavior of simple correlations [33,34] led to the development of ''mode-coupling'' theories. The seminal work of Kawasaki [35], who proposed that the linear Langevin equation be replaced by a nonlinear version in which the fluctuating forces obey Gaussian statistics, sparked the later development of kinetic mode-coupling theory models of dense liquids [36–40]. At roughly the same time, Ronis [41] used the framework of the Kawasaki mode-coupling theory to formulate a theory of higher-order correlation functions in which the multilinear slow variables forming the basis set for long-time evolution in the system obey Gaussian statistics. Although Ronis's theory contains a number of assumptions, it is the assumption of Gaussian statistics, which leads to clear inconsistencies in the predictions for higher-order correlation functions. Unfortunately, the Gaussian assumption is fundamental in Kawasaki's formulation of mode-coupling theory, and is difficult to generalize.

The purpose of this paper is to provide a solid theoretical framework to calculate multiple-point and multiple-time correlation functions. It is based on the mode-coupling theory obtained by a projection operator formalism [42,43] as developed by Oppenheim and co-workers [44–47]. By careful consideration of how to consistently identify fast and slow behavior in time correlation functions, we derive expressions for multiple-point and multiple-time correlation functions in terms of simple time correlation functions. Since the basis set for the slow modes is infinite, an infinite number of terms arise in the expressions for the higher-order correlation functions. It is demonstrated that if the system has a finite correlation length, the infinite series can be truncated by applying the so-called N-ordering perturbation expansion method, which is exact in the thermodynamic limit. The use of this perturbation scheme circumvents the need to assume that the basis set obeys Gaussian statistics. Based on this method, the leading-order expressions and first mode-coupling corrections for higher-order correlation functions are presented. Finally, it is shown how the formalism applies for an ideal gas system, for which it is demonstrated that the theory yields the exact result for simple, multiple-point, and multiple-time correlation functions.

II. TWO-TIME CORRELATIONS

A. The system and slow variables

Consider a classical system composed of N point particles in which the momentum and position of particle i are denoted by $\mathbf{p}_i$ and $\mathbf{r}_i$, respectively. Given the Hamiltonian $\mathcal{H}$, a function $B(\Gamma)$ of the phase point $\Gamma=(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)$ evolves according to

$$\dot{B}(t)=\{B(t),\mathcal{H}\}\equiv\mathcal{L}B(t),$$

where {,} denotes the Poisson bracket and $\mathcal{L}$ is the Liouville operator for the system. The evolution equation can be solved formally as $B(t)=\exp(\mathcal{L}t)B(0)$, where here and below $B(t)$ is taken to denote $B(\Gamma(t))$.

Typically, each dynamical variable of the system can be separated into slowly varying and quickly varying parts. We will assume that the time-dependent correlation functions of the quickly varying components decay to zero on a short (called ''microscopic'') time scale τ_m, whereas correlation functions of the slowly varying part decay on a longer time scale τ_h. Hence, at long times $t\gg\tau_m$, the decay of an arbitrary correlation function can be described by the decay of its slow component. In what follows, we postulate that the slowly varying part of an arbitrary dynamical variable is an analytic function of a set of slow variables of the system. In this sense, the slow variables form a basis set in which to represent the long-time behavior of the system.

To identify slow variables in such a system, one considers all the conserved quantities, which can be taken together in one column vector A, with components A^a. When these quantities are extensive, they can be expressed as a sum over contributions from the individual particles,

$$A(\Gamma)=\sum_{j=1}^{N}a_j(\Gamma), \tag{1}$$

which leads to the identification of the densities as the local version of A,

$$A(\mathbf{r};t)=\sum_j a_j(t)\,\delta(\mathbf{r}-\mathbf{r}_j(t)), \tag{2}$$

with Fourier components

$$A_{\mathbf{k}}(t)=\sum_j a_j(t)e^{i\mathbf{k}\cdot\mathbf{r}_j(t)}. \tag{3}$$

For the case of a simple fluid of N point particles, the extensive slow variables are the number density, momentum density, angular momentum density and the energy density, and in Eq. (2), one would use the microscopic expressions for those quantities. For point particles, the angular momentum density can be expressed in terms of the momentum density and need not be included in A.

The small wave-vector components $A_{\mathbf{k}}$ of the densities correspond to large length scale fluctuations, and these are expected to evolve slowly since their time derivatives are proportional to $|\mathbf{k}|$. On the other hand, large wave vectors with magnitudes beyond some cutoff value k_c correspond to small length-scale fluctuations and have large time derivatives provided the system is not too dense. Thus, one can identify the slow variables to be composed of the Fourier transform of densities of conserved variables whose wave-vector arguments $\mathbf{k}_i$ are restricted and have magnitudes less than k_c.

B. Generalized Langevin equation

The distinction between fast and slow behavior can be made more precise on the level of correlation functions, following the projection operator method as used by Oppenheim and co-workers [44–47].

To isolate the slow part of a correlation function, one assumes it to be an analytic function of the slow variables $A_{\mathbf{k}}$. The nonlinear dependence of the time correlation functions on the slow variables can be incorporated within the framework of projection techniques by employing a basis of nonlinear functions of $A_{\mathbf{k}}$, the so-called multilinear basis.

Using the ensemble average $\langle\cdots\rangle$ as an inner product, we define a projection operator $\mathcal{P}_1$ that projects onto the deviations $\hat{A}_{\mathbf{k}}\equiv A_{\mathbf{k}}-\langle A_{\mathbf{k}}\rangle$ of the slow variables from their equilibrium value as

$$\mathcal{P}_1 X \equiv \langle X\hat{A}_{\mathbf{k}}\rangle * K_{\mathbf{k}}^{-1} * \hat{A}_{\mathbf{k}}, \tag{4}$$

where

$$K_{\mathbf{k}} = \langle \hat{A}_{\mathbf{k}} \hat{A}^*_{\mathbf{k}}\rangle$$

denotes the normalization. The "$*$" product in Eq. (4) includes a sum over components of the column vector $A_{\mathbf{k}}$—the *hydrodynamic indices*—as well as over wave vectors $\mathbf{k}$. For a translationally invariant system, all wave vectors in an average must add to zero, so only when $\mathbf{k}$ equals the sum of wave vectors in X will there be a contribution in Eq. (4).

Using only the linear projection $\mathcal{P}_1$ will not give a proper mode-coupling theory since the long-time dependence of dynamical variables due to multilinear orders of the densities is not extracted by the projection operator [46–49]. It is therefore convenient to define an orthogonal, multilinear basis as

$$Q_0 \equiv 1,$$

$$Q^a_{\mathbf{k}} \equiv A^a_{\mathbf{k}} - \mathcal{P}_0 A^a_{\mathbf{k}} \equiv \hat{A}^a_{\mathbf{k}},$$

$$Q^{a,b}_{\mathbf{k}-\mathbf{q},\mathbf{q}} \equiv \hat{A}^a_{\mathbf{k}-\mathbf{q}} \hat{A}^b_{\mathbf{q}} - (\mathcal{P}_0+\mathcal{P}_1)\hat{A}^a_{\mathbf{k}-\mathbf{q}} \hat{A}^b_{\mathbf{q}},$$

$$\vdots$$

$$Q^{a_1,a_2,\ldots,a_n}_{\mathbf{k}_1-\mathbf{k}',\mathbf{k}_2,\ldots,\mathbf{k}_n} \equiv \left[\mathbb{1} - \sum_{j=0}^{n-1} \mathcal{P}_j\right] \hat{A}^{a_1}_{\mathbf{k}_1-\mathbf{k}'} \hat{A}^{a_2}_{\mathbf{k}_2} \cdots \hat{A}^{a_n}_{\mathbf{k}_n}, \tag{5}$$

where $\mathbf{k}' = \Sigma_{l=2}^{n} \mathbf{k}_l$, and the projection operators $\mathcal{P}_j$ are defined as

$$\mathcal{P}_j X = \sum_{|\alpha|=j} \langle X Q_{\hat{\alpha}}\rangle * K^{-1}_{\hat{\alpha}\alpha} * Q_\alpha . \tag{6}$$

In this notation, a Greek index denotes a set of wave vectors and hydrodynamic indices, and $|\alpha|$ denotes the number, or *mode order*, of hydrodynamic indices in a set α. For simplicity of notation, the full notation will often be written Q_1, Q_2, Q_3, etc., for Q_α when $|\alpha| = 1,2,3,\ldots$. Furthermore, nonhatted and hatted Greek indices will always have the same mode order, i.e., $|\alpha| = |\hat{\alpha}|$, but represent different sets of wave vectors and/or hydrodynamic indices. Finally, in Eq. (6) $K_{\hat{\alpha}\alpha} = \langle Q_{\hat{\alpha}} Q_\alpha\rangle$ and the "$*$" product now includes a sum over all hydrodynamic indices and wave vectors in the summation indices (α and $\hat{\alpha}$). To make sure the contributions from the same component in a sum over α are not overcounted, one has to divide by the number of ways the indices can be rearranged in α.

The projection terms in Eq. (5) force the set Q_α to be orthogonal in mode order so that $\langle Q_\alpha Q_\beta\rangle = 0$ unless $|\alpha| = |\beta|$. This property will be not only convenient but very important in the subsequent analysis. By assumption, the long-time behavior of an arbitrary variable C can be isolated by the projection operator,

$$\mathcal{P}C \equiv \sum_{j=0}^{\infty} \mathcal{P}_j C = \langle C Q^*_\alpha\rangle K^{-1}_{\alpha\hat{\alpha}} Q_{\hat{\alpha}}, \tag{7}$$

where we have used the convention that repeated Greek indices imply a "$*$" product and a summation over mode order. This notation will be used throughout this article unless stated otherwise.

Applying operator identity

$$e^{At} = e^{(A+B)t} - \int_0^t e^{A(t-\tau)} B e^{(A+B)\tau} d\tau$$

to the evolution equation, one easily obtains

$$e^{\mathcal{L}t} = e^{\mathcal{L}t}\mathcal{P} + e^{\mathcal{L}_\perp t}\mathcal{P}_\perp + \int_0^t e^{\mathcal{L}(t-\tau)} \mathcal{P}\mathcal{L} e^{\mathcal{L}_\perp \tau} \mathcal{P}_\perp d\tau, \tag{8}$$

where $\mathcal{P}_\perp = 1 - \mathcal{P}$ and $\mathcal{L}_\perp = \mathcal{P}_\perp \mathcal{L}$. We apply this operator to $\dot{Q}_\alpha$, and write out $\mathcal{P}$ to get

$$\begin{aligned}\dot{Q}_\alpha(t) &= \langle \dot{Q}_\alpha Q^*_\beta\rangle K^{-1}_{\beta\hat{\beta}} Q_{\hat{\beta}}(t) + \phi_\alpha(t)\\ &\quad + \int_0^t e^{\mathcal{L}(t-\tau)} \langle Q^*_\beta \mathcal{L} e^{\mathcal{L}_\perp \tau} \mathcal{P}_\perp \dot{Q}_\alpha\rangle K^{-1}_{\beta\hat{\beta}} Q_{\hat{\beta}} d\tau\\ &= \int_0^t M_{\alpha\beta}(\tau) Q_\beta(t-\tau) d\tau + \phi_\alpha(t),\end{aligned} \tag{9}$$

which is the generalized Langevin equation, where

$$M_{\alpha\beta}(\tau) \equiv [2\delta(\tau)\langle \dot{Q}_\alpha Q^*_{\hat{\beta}}\rangle - \langle \phi_\alpha(\tau)\phi^*_{\hat{\beta}}\rangle] K^{-1}_{\hat{\beta}\beta}, \tag{10}$$

and the fluctuating force $\phi_\alpha(t)$ is defined by

$$\phi_\alpha(t) \equiv e^{\mathcal{L}_\perp t} \mathcal{L}_\perp Q_\alpha = e^{\mathcal{L}_\perp t} \mathcal{P}_\perp \dot{Q}_\alpha . \tag{11}$$

Under the assumption that $\mathcal{P}$ projects out all the slow behavior, the matrix $M_{\alpha\beta}(\tau)$ is "fast" in the time variable τ in the sense that, for a microscopic time scale τ_m much smaller then the hydrodynamic time scale τ_h of the slow variables,

$$\langle \phi_\alpha(\tau) B\rangle \simeq \int_0^\infty \langle \phi_\alpha(t) B\rangle dt\, \delta(\tau) + O(\tau_m/\tau_h). \tag{12}$$

It then follows that the main contribution in the integral in Eq. (9) comes from small τ, and we can approximate Eq. (9) by one that is local in time,

$$\dot{Q}_\alpha(t)=\overline{M}_{\alpha\beta}Q_\beta(t)+\phi_\alpha(t), \tag{13}$$

where the instantaneous matrix is given by

$$\overline{M}_{\alpha\beta}=\int_0^\infty M_{\alpha\beta}(t)dt. \tag{14}$$

It will become clear in Sec. II E that the assumption of a fast decaying memory kernel in Eq. (9) is not in contradiction with the slow memory kernel that occurs in *linear* mode-coupling equations like those used in the study of the glass transition [36].

Defining the time correlation functions of the basis set to be

$$G_{\alpha\beta}(t)\equiv\langle Q_\alpha(t)Q^*_{\hat{\beta}}\rangle K^{-1}_{\hat{\beta}\beta}, \tag{15}$$

and using Eq. (9), one obtains the simple expression for the time correlation function,

$$\dot{G}_{\alpha\beta}(t)=\int_0^t M_{\alpha\delta}(\tau)G_{\delta\beta}(t-\tau)d\tau, \tag{16}$$

where we have used the fact that $\langle\phi_\alpha(t)Q^*_\beta\rangle=0$ by construction.

In the instantaneous approximation [corresponding to Eq. (12)], Eq. (13) yields $\dot{G}_{\alpha\beta}(t)=\overline{M}_{\alpha\delta}G_{\delta\beta}(t)$, which can be integrated to obtain

$$G_{\alpha\beta}(t)=[e^{\overline{M}t}]_{\alpha\beta}. \tag{17}$$

If we do not wish to make the instantaneous approximation, it is easiest to look at the Laplace transform of the time correlation function

$$G_{\alpha\beta}(z)\equiv\int_0^\infty G_{\alpha\beta}(t)e^{-zt}dt.$$

Since the time convolution in Eq. (16) is a simple product in Laplace space, we have

$$G_{\alpha\beta}(z)=\langle Q_\alpha(z)Q^*_{\hat{\beta}}\rangle K^{-1}_{\hat{\beta}\beta}=[z\mathbb{1}-M(z)]^{-1}_{\alpha\beta}, \tag{18}$$

where the $\alpha\beta$ element of the inverse is meant, and $M_{\alpha\beta}(z)=[\langle\dot{Q}_\alpha Q^*_{\hat{\beta}}\rangle-\langle\phi_\alpha(z)\phi^*_{\hat{\beta}}\rangle]K^{-1}_{\hat{\beta}\beta}$.

Note that one is frequently interested in just the part of $G_{\alpha\beta}(t)$ that involves the linear variables, corresponding to such readily observable physical quantities as the time correlation functions of the linear density, momentum, and energy. These are given by $G_{11}(t)$, the $|\alpha|=|\beta|=1$ sub-block of the infinite-dimensional matrix $G_{\alpha\beta}(t)$.

In the hydrodynamic limit in which the magnitude of the wave vectors $\mathbf{k}$ is small, the wave vector can be used to perturbatively order various contributions to $M_{\alpha\beta}(z)$. Noting that each time derivative in Eq. (10) brings down a factor of $\mathbf{k}$, the first term in Eq. (10), called the *Euler* term, is of order $\mathbf{k}$, whereas the second, or *dissipative* term, is $O(|\mathbf{k}|^2)$. On the basis of these arguments, one might think that the dissipative term in $M_{\alpha\beta}(z)$ can be neglected in the hydrodynamic limit. However, examining the form of the densities, it is easy to see that in fact the Euler term is imaginary and can only give rise to oscillatory behavior.[1] It is therefore clear that the dissipative term must be included in order to obtain solutions to Eq. (13), which are well behaved in the long-time limit.

C. *N* ordering

Since two-time correlation functions at a particular mode order are given by specific blocks of the inverse of an infinite-dimensional matrix, even the calculation of simple time correlation functions requires an infinite number of multilinear modes. Thus, the results of the previous section are formally exact, but not very useful.

The evaluation of the time correlation functions is greatly facilitated by applying cumulant expansion or *N*-ordering techniques. The *N*-ordering scheme was first introduced by Machta and Oppenheim [44] as an extension of van Kampen's inverse system size expansion (Ω expansion) [50] and developed further in Ref. [46]. It is essential in obtaining the correct Stokes-Einstein law for a Brownian particle using mode-coupling techniques [47].

In the *N*-ordering approach, one assigns to each cumulant of an average appearing in the equations an order of N (the number of particles). The starting point is to consider cumulants, which we denote by "$\langle\langle\cdots\rangle\rangle$." For a product of linear densities, the cumulant expansion consists of all possible ways of combining the densities into groups, i.e., $\langle A\rangle=\langle\langle A\rangle\rangle$, $\langle AB\rangle=\langle\langle AB\rangle\rangle+\langle\langle A\rangle\rangle\langle\langle B\rangle\rangle$, and so on. The assignment of N orders is based on the observation that each cumulant containing n linear densities is of order $N(\xi/a)^{3(n-1)}$, where a is the average distance between particles [44]. Hence, the requirements for the expansion method to be meaningful are that the system should have a finite $[O(N^0)]$ correlation length ξ, and that the integrated densities should be extensive. For an extension to nonextensive quantities like tagged particle densities, see Ref. [47].

For instance, the cumulant of a linear-linear correlation function of the number density $N_{\mathbf{k}}$, defined as $\Sigma_{j=1}^N e^{i\mathbf{k}\cdot\mathbf{r}}$, can be formally written as

$$\langle\langle N_{\mathbf{k}}N^*_{\mathbf{k}}\rangle\rangle=\langle N_{\mathbf{k}}N^*_{\mathbf{k}}\rangle-\langle N_{\mathbf{k}}\rangle\langle N^*_{\mathbf{k}}\rangle\delta_{k0}.$$

$$=[\langle N\rangle+\langle N(N-1)e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)}\rangle](1-\delta_{\mathbf{k}0})$$
$$+[\langle N^2\rangle-\langle N\rangle^2]\delta_{\mathbf{k}0}.$$

For $\mathbf{k}=0$, the cumulant expansion of $\langle N_{\mathbf{k}}N^*_{\mathbf{k}}\rangle$ is given by $\langle(N-\langle N\rangle)^2\rangle$, which, in the grand canonical ensemble, is of order $\langle N\rangle$. For $\mathbf{k}\neq0$, the expression is proportional to N as

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[1] The Euler term can give rise to Gaussian relaxation if one has an infinite number of slow modes, see Sec. V.

well, because particles beyond the correlation length ξ will not contribute to the average of $\exp[i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)]$, so that

$$\langle N(N-1)\exp[i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)]\rangle\propto N(N-1)\frac{\xi^3}{V}=O(N).$$

The N ordering of various quantities has been discussed extensively elsewhere [44,46,47], so here we just state a few properties of the procedure that enable us to estimate N orders of relevant quantities.

One important basic property of averages involving Q_α is that when one has an average of the form $\langle Q_\alpha(t)BQ_1^*\rangle$, where B can be a product of Q_1 again, it can be factored into a term of order N^2,

$$\langle Q_\alpha(t)BQ_{\mathbf{k}}^{a*}\rangle\approx\langle Q_{\alpha-1}(t)B\rangle\langle Q_{\mathbf{k}_j}^{a_j}(t)Q_{\mathbf{k}}^{a*}\rangle\delta_{\mathbf{k}_j\mathbf{k}} \tag{19}$$

along with terms involving lower powers of N, provided that the *time-dependent* correlation length is not extensive. Hence the leading N-order term in the cumulant expansion can be found by equating any wave vector $\mathbf{k}_j$ from the set α with $\mathbf{k}$. In Eq. (19), $\alpha-1$ denotes the set α with $\mathbf{k}_j$ and a_j removed, and "$\approx$" means that the expression is correct up to higher orders of N and only for the case where appropriate wave vectors have been equated. The importance of correction terms to the leading-order factorization of time-dependent correlation functions is discussed in greater detail in the following section. We can reduce such an expression further by equating wave vectors in B with those in the set $\alpha-1$. An important point, established in Ref. [46], is that equating wave vectors within the set α does not increase the N order due to the subtraction terms in their definition Eq. (5). Thus the orthogonalization procedure used to construct the multilinear basis plays an important role in the proper N ordering of correlation functions of multilinear densities.

Using the ordering scheme, one obtains $K_{\alpha\hat{\alpha}}=O(N^j)$, where j is the number of matched sets of wave vectors in α and $\hat{\alpha}$, and hence the N ordering of its inverse is

$$K_{\alpha\hat{\alpha}}^{-1}=O(N^{-|\alpha|}), \tag{20}$$

irrespective of the matching of wave vectors. In Ref. [44], it was shown that

$$M_{\alpha\beta}(t)=\begin{cases}O(1) & \text{if } |\alpha|\geqslant|\beta|,\\ O(N^{|\alpha|-|\beta|}) & \text{if } |\alpha|<|\beta|,\end{cases}$$

with the same N ordering holding for $\overline{M}_{\alpha\beta}$. A similar result can be obtained for $G_{\alpha\beta}(t)$,

$$G_{\alpha\beta}(t)=\begin{cases}O(1) & \text{if } |\alpha|\geqslant|\beta|,\\ O(N^{|\alpha|-|\beta|}) & \text{if } |\alpha|<|\beta|.\end{cases} \tag{21}$$

D. Multiple-point correlations

We define a multiple-point correlation function to be any $G_{\alpha\beta}(t)$ for which $|\alpha|$ or $|\beta|$ is greater than 1. The multiple-point correlations functions therefore contain several factors of the linear densities $A_{\mathbf{k}}$, and involve more than one wave vector. Hence, in position space, the multiple-point correlation functions involve at least three spatial, or *two relative*, position coordinates, justifying the name multiple-point correlation functions.

As $M_{\alpha\beta}(z)$ is $O(1)$ if α and β have all wave vectors matched, and of lower order otherwise, the leading N-order contributions to $G_{\alpha\beta}(t)$ can be obtained by expanding Eq. (18) in the wave-vector-diagonal component of $M_{\alpha\beta}(z)$, denoted by $M^d_{\alpha\beta}=M_{\alpha\alpha'}(z)\delta_{\alpha'\beta}$. Here primed Greek indices will always have the same set of wave vectors as their unprimed variant, but not necessarily the same hydrodynamic indices. Defining the off-diagonal part as $M^o_{\alpha\beta}(z)=M_{\alpha\beta}(z)-M_{\alpha\alpha'}(z)\delta_{\alpha'\beta}$, we get from Eq. (18),

$$\begin{aligned}G_{\alpha\beta}(z)&=[z\mathbb{1}-M^d(z)-M^o(z)]^{-1}_{\alpha\beta}\\&=[\{z\mathbb{1}-M^d(z)\}\{\mathbb{1}-\hat{G}(z)M^o(z)\}]^{-1}_{\alpha\beta}\\&=[\mathbb{1}-\hat{G}(z)M^o(z)]^{-1}_{\alpha\beta'}\hat{G}_{\beta'\beta}(z),\end{aligned} \tag{22}$$

where we have defined the diagonal in the wave vector as

$$\hat{G}_{\alpha\alpha'}(z)=[z\mathbb{1}-M^d(z)]^{-1}_{\alpha\alpha'}. \tag{23}$$

We can therefore expand Eq. (22) as

$$\begin{aligned}G_{\alpha\beta}(z)={}&\hat{G}_{\alpha\alpha'}(z)\delta_{\alpha'\beta}+\hat{G}_{\alpha\alpha'}(z)M^o_{\alpha'\beta'}(z)\hat{G}_{\beta'\beta}(z)\\&+\hat{G}_{\alpha\alpha'}(z)M^o_{\alpha'\gamma}(z)\hat{G}_{\gamma\gamma'}(z)M^o_{\gamma'\beta'}(z)\hat{G}_{\beta'\beta}(z)\\&+\cdots.\end{aligned} \tag{24}$$

Note that when a term is of lower order in N, this does not mean it can be neglected in the thermodynamic limit. The leading N order is found from equating wave vectors, whereas the next order in N often comes with an unrestricted summation over wave vectors. If M denotes the number of (slow) wave vectors in the system, these correction terms are $O(M/N)$. The number of wave vectors M grows with the system size. Therefore, such mode-coupling corrections survive in the thermodynamic limit.

The magnitude of the order parameter $M/N\sim k_c\xi$ is determined by two length scales. The first length scale $\sim k_c^{-1}$ corresponds to the smallest length scale for which the evolution of the densities in the basis set is slow. The other length scale ξ is determined by the correlation length of the possibly time-dependent correlation function under consideration. Both length scales change dramatically with density in dense liquids due to the emergence of slowly evolving short-wavelength collective modes [51] and the cooperative movement of particles in the fluid [2,52]. Under these circumstances, the mode-coupling expansion in powers of M/N is not well defined and can only be interpreted as a formal series. On the other hand, for systems of low to moderate density, one can anticipate that time-dependent correlations are short ranged on all time scales and that k_c is small. For such systems, M/N can be treated as a perturbation parameter [46]. Nonetheless, it should be emphasized that the projection operator formalism presented here relies on a clear separation of time scales between the slow variables and all other dynamical properties in the system. For hydrodynamic densities (of small k), this separation between microscopic and "hydrodynamic" time scales is evident, whereas physical arguments must be invoked for other systems to establish the necessary separation of time scales.

In Eq. (24), note the appearance of $\hat{G}_{\alpha\alpha'}$ defined in Eq. (23). Although this is diagonal in the wave vector, it is *not* the diagonal part of $G_{\alpha\beta}$, as the terms following the first term in Eq. (24) give contributions for α and β diagonal. As was shown in Ref. [46], in the thermodynamic limit, the diagonal part of $G_{\alpha\beta}$, denoted by $G_{\alpha\alpha'}$, can be factored as

$$G_{\alpha\alpha'}(t)\approx\sum_{\sigma}\left[\prod_{j} G^{a_j a'_j}_{\mathbf{k}_j}(t),\delta_{\mathbf{k}_j\mathbf{k}'_{\sigma_j}}\right], \tag{25}$$

where a_j and a'_{σ_j} are hydrodynamic indices from α and α', and $\mathbf{k}_j$ and $\mathbf{k}'_{\sigma_j}$ are the respective wave vectors. The summation is over all permutations σ of the indices in α'. This factorization is obtained also by cumulant expansion under the assumption that there is a finite time-dependent correlation length.

Thus, if we were able to express Eq. (24) in terms of $G_{\alpha\alpha'}$ instead of $\hat{G}_{\alpha\alpha'}$, we could combine that with Eq. (25) to get an expression for any multiple-point function in terms of in the two-point correlation functions G_{11} and vertices $M^{o}_{\alpha\beta}$. Equation (24) can be reexpressed in this desired form by the following resummation of terms: We write $G_{\alpha\beta}=G_{\alpha\alpha'}\delta_{\alpha'\beta}+G^{0}_{\alpha\beta}$, and use the Dyson form of Eq. (24),

$$G_{\alpha\beta}=\hat{G}_{\alpha\alpha'}\delta_{\alpha'\beta}+G_{\alpha\gamma}M^{o}_{\gamma\beta'}\hat{G}_{\beta'\beta},$$

for the off-diagonal part to get

$$G_{\alpha\beta}=G_{\alpha\alpha'}\delta_{\alpha'\beta}+G_{\alpha\gamma}M^{o}_{\gamma\beta'}\hat{G}^{(\alpha)}_{\beta'\beta},$$

where the superscript (α) means that β is restricted to not have the same wave-vector set as α. Iterating this equation yields

$$\begin{aligned}G_{\alpha\beta}&=G_{\alpha\alpha'}\delta_{\alpha'\beta}+G_{\alpha\alpha'}M^{o}_{\alpha'\beta'}\hat{G}^{(\alpha)}_{\beta'\beta}\\&\quad+G_{\alpha\alpha'}M^{o}_{\alpha'\gamma'}\hat{G}^{(\alpha)}_{\gamma'\gamma}M^{o}_{\gamma\beta'}\hat{G}^{(\alpha)}_{\beta'\beta}+\cdots\\&\equiv G_{\alpha\alpha'}\delta_{\alpha'\beta}+G_{\alpha\alpha'}M^{o}_{\alpha'\delta}\tilde{G}^{(\alpha)}_{\delta\beta},\end{aligned}$$

where by definition, $\tilde{G}^{(\alpha)}_{\delta\beta}$ has the same form as the right-hand side of Eq. (24), with α replaced by δ and the restriction that none of the wave-vector sets in the expression are equal to α. Being of that form, we can repeat this procedure for $\tilde{G}^{(\alpha)}_{\delta\beta}$ to obtain

$$\begin{aligned}G_{\alpha\beta}&=G_{\alpha\alpha'}\delta_{\alpha'\beta}+G_{\alpha\alpha'}M^{o}_{\alpha'\delta}\tilde{G}^{(\alpha)}_{\delta\beta}\\&\quad+G_{\alpha\alpha'}M^{o}_{\alpha'\gamma}\tilde{G}^{(\alpha)}_{\gamma\gamma'}M^{o}_{\gamma'\delta}\tilde{G}^{(\alpha,\gamma)}_{\delta\beta}.\end{aligned}$$

When the procedure is continued *ad infinitum*, we find

$$\begin{aligned}G_{\alpha\beta}&=G_{\alpha\alpha'}\delta_{\alpha'\beta}+G_{\alpha\alpha'}M^{o}_{\alpha'\beta'}\tilde{G}^{(\alpha)}_{\beta'\beta}\\&\quad+G_{\alpha\alpha'}M^{o}_{\alpha'\delta}\tilde{G}^{(\alpha)}_{\delta\delta'}M^{o}_{\delta'\beta'}\tilde{G}^{(\alpha,\delta)}_{\beta'\beta}\\&\quad+G_{\alpha\alpha'}M^{o}_{\alpha'\delta}\tilde{G}^{(\alpha)}_{\delta\delta'}M^{o}_{\delta'\gamma}\tilde{G}^{(\alpha,\delta)}_{\gamma\gamma'}M^{o}_{\gamma'\beta'}\tilde{G}^{(\alpha,\delta,\gamma)}_{\beta'\beta}+\cdots.\end{aligned}$$

This expression resembles that for $G_{\alpha\alpha'}$ in Eq. (24) with $\beta=\alpha'$ and $\hat{G}_{\gamma\gamma'}$ replaced by $\tilde{G}^{(\alpha,\dots)}_{\gamma\gamma'}$. Furthermore, the definition of $\tilde{G}^{(\alpha,\dots)}_{\gamma\gamma'}$ also resembles the definition of $G_{\gamma\gamma'}$, but now with restrictions on all wave-vector sets. In fact the wave-vector restrictions can be relaxed in the thermodynamic limit since the restrictions remove only one term out of the sum over intermediate wave vectors. Relatively speaking, the difference between the series with restricted and unrestricted sums is of order $O(1/N)$, so the restriction on the intermediate wave vectors is negligible in the thermodynamic limit, and we can write

$$\tilde{G}^{(\alpha,\dots)}_{\beta\beta'}=G^{(\alpha,\dots)}_{\beta\beta'},$$

where $\tilde{G}^{(\alpha,\dots)}_{\beta\beta'}$ is the full correlation function that is diagonal in the wave vector and in which the set of wave vectors in β differ from those in sets in $\alpha,\dots$.

Thus Eq. (24), which has a nonphysical $\hat{G}$, can be replaced by the expansion

$$\begin{aligned}G_{\alpha\beta}&=G_{\alpha\alpha'}\delta_{\alpha'\beta}+G_{\alpha\alpha'}M^{o}_{\alpha'\beta'}G^{(\alpha)}_{\beta'\beta}\\&\quad+G_{\alpha\alpha'}M^{o}_{\alpha'\delta}G^{(\alpha)}_{\delta\delta'}M^{o}_{\delta'\beta'}G^{(\alpha,\delta)}_{\beta'\beta}\\&\quad+G_{\alpha\alpha'}M^{o}_{\alpha'\delta}G^{(\alpha)}_{\delta\delta'}M^{o}_{\delta'\gamma}G^{(\alpha,\delta)}_{\gamma\gamma'}M^{o}_{\gamma'\beta'}G^{(\alpha,\delta,\gamma)}_{\beta'\beta}+\cdots,\end{aligned} \tag{26}$$

which involves the full correlation function $G_{\alpha\alpha'}$ which is diagonal in the wave vector. In this expression none of the intermediate wave-vector sets are allowed to be equal.

Using Eq. (26), we can write to leading N order,

$$G_{12}(z)=G_{11}(z)*M_{12}(z)*G_{22}(z), \tag{27}$$

where, from Eq. (25), the diagonal $G_{22}(t)$ is given by

$$\begin{aligned}&G^{22}_{\mathbf{k}-\mathbf{q}',\mathbf{q}';\mathbf{k}-\mathbf{q},\mathbf{q}}(t)(\delta_{\mathbf{q},\mathbf{q}'}+\delta_{\mathbf{k}-\mathbf{q}',\mathbf{q}})\\&\quad\approx G^{11}_{\mathbf{k}-\mathbf{q}}(t)\cdot G^{11}_{\mathbf{q}}(t)\,\delta_{\mathbf{q},\mathbf{k}-\mathbf{q}'}+G^{11}_{\mathbf{k}-\mathbf{q}}(t)\circ G^{11}_{\mathbf{q}}(t)\,\delta_{\mathbf{q}\mathbf{q}'},\end{aligned} \tag{28}$$

where superscripts like 22 and 11 are a reminder of the mode orders of the arguments. In order to facilitate writing tensor products, we have introduced the following notational symbols for products of tensors of rank 2 ($A^{a;b}$), rank 3 ($A^{a;bc}$ if b and c belong to the same set α or $A^{ab;c}$ if a and b belong to the same set), or rank 4 (such as $A^{a,b;c,d}$):

$$(A\cdot B)^{a;c}\equiv A^{a;b}B^{b;c},$$

$$(A:B)^{a;c}\equiv A^{a;d,f}B^{d,f;c},$$

$$(SA)^{ab;c} \equiv A^{c;ba},$$

$$(A \circ B)^{a,b;c,d} \equiv A^{a;c} B^{b;d},$$

$$(A \bullet B)^{a,b;c,d} \equiv A^{a;d} B^{b;c}, \tag{29}$$

where repeated labels are summed over.

The two terms in the expression above for G_{22} turn out to yield the same contribution to G_{12} in Eq. (27). However, this summation has a prefactor of 1/2 from the number of ways the indices can be interchanged in the "*" product. Using Eq. (28) in Eq. (27), we obtain

$$G^{12}_{\mathbf{k};\mathbf{k}-\mathbf{q},\mathbf{q}}(t) = \int_0^t G^{11}_{\mathbf{k}}(t-\tau) \cdot \overline{M}^{12}_{\mathbf{k};\mathbf{k}-\mathbf{q},\mathbf{q}} : [G^{11}_{\mathbf{k}-\mathbf{q}}(\tau) \circ G^{11}_{\mathbf{q}}(\tau)] d\tau, \tag{30}$$

where the time convolution arises from the inverse Laplace transform.

At this point, the necessity of including multilinear modes is readily apparent. For example, using the definition of the multilinear basis set, we can write

$$\langle Q_1(t) Q_1^* Q_1^* \rangle = \langle Q_1(t) Q_1^* \rangle * K_{11}^{-1} * \langle Q_1 Q_1^* Q_1^* \rangle + G_{12}(t) * K_{22} \tag{31}$$

and note that the second term would have been absent if the bilinear modes Q_2 in the basis set had not been included even though the N ordering of this term is the same as the first term. Another interesting point is that the first term is not present if the subtractions in the definition of Q_2 in the basis set are not included. If one assumes that the Q_1 are Gaussian random variables, then correlations of the form $\langle Q_1 Q_1^* Q_1^* \rangle$ vanish. However, in dense fluids the linear densities clearly do not obey Gaussian statistics since static correlations such as $\langle Q_1 Q_1^* Q_1^* \rangle$ involve configurational averages over the triplet distribution function and are not negligible. Note that the second term involves a time convolution in Eq. (30) and can be expected to have quite different behavior from the first term, which is proportional to an ordinary time correlation function.

E. Renormalization of the propagator

In this section we focus on the linear correlation function G_{11} itself. Equation (24) for $G_{11}(z)$ reads

$$\begin{aligned} G_{11} = {} & \hat{G}_{11} + \hat{G}_{11} M^o_{1\alpha} \hat{G}_{\alpha\alpha'} M^o_{\alpha'1} \hat{G}_{11} \\ & + \hat{G}_{11} M^o_{1\alpha} \hat{G}_{\alpha\alpha'} M^o_{\alpha'\beta'} \hat{G}_{\beta'\beta} M^o_{\beta 1} \hat{G}_{11} \\ & + \hat{G}_{11} M^o_{1\alpha} \hat{G}_{\alpha\alpha'} M^o_{\alpha'\beta'} \hat{G}_{\beta'\beta} M^o_{\beta\gamma} \hat{G}_{\gamma\gamma'} M^o_{\gamma'1} \hat{G}_{11} + \cdots, \end{aligned}$$

where for brevity we have omitted the z argument. In the summations over α, one can isolate all the terms with mode order 1 to obtain

$$\begin{aligned} G_{11} = {} & \hat{G}_{11} + \hat{G}_{11} (M^o_{1\alpha} \hat{G}_{\alpha\alpha'} M^o_{\alpha'1}) \hat{G}_{11} \\ & + \hat{G}_{11} (M^o_{1\alpha} \hat{G}_{\alpha\alpha'} M^o_{\alpha'\beta'} \hat{G}_{\beta'\beta} M^o_{\beta 1}) \hat{G}_{11} \\ & + \hat{G}_{11} (M^o_{1\alpha} \hat{G}_{\alpha\alpha'} M^o_{\alpha'\beta'} \hat{G}_{\beta'\beta} M^o_{\beta\gamma} \hat{G}_{\gamma\gamma'} M^o_{\gamma'1}) \hat{G}_{11} \\ & + \hat{G}_{11} (M^o_{1\alpha} \hat{G}_{\alpha\alpha'} M^o_{\alpha'1}) \hat{G}_{11} (M^o_{1\gamma} \hat{G}_{\gamma\gamma'} M^o_{\gamma'1}) \hat{G}_{11} + \cdots, \end{aligned}$$

where the summation over repeated indices here start at mode order 2. Rearranging the terms, this can be written as

$$G_{11} = \hat{G}_{11} + \hat{G}_{11} * \Sigma_{11} * \hat{G}_{11} + \hat{G}_{11} * \Sigma_{11} * \hat{G}_{11} * \Sigma_{11} * \hat{G}_{11} + \cdots, \tag{32}$$

with

$$\Sigma_{11} = \sum_{i=1}^{\infty} \Theta_i,$$

$$\Theta_1 = \sum_{|\alpha| \neq 1} M^0_{1\alpha} * \hat{G}_{\alpha\alpha'} * M^0_{\alpha'1},$$

$$\Theta_2 = \sum_{|\alpha| \neq 1, |\beta| \neq 1} M^0_{1\alpha} * \hat{G}_{\alpha\alpha'} * M^0_{\alpha'\beta'} * \hat{G}_{\beta'\beta} * M^0_{\beta 1},$$

$$\cdots. \tag{33}$$

Equation (32) can be resummed as

$$G_{11}(z) = [z\mathbb{1} - M_{11} - \Sigma_{11}(z)]^{-1}, \tag{34}$$

where the inverse is taken on the 11 sub-block level. Equation (34) can be utilized to extract the complicated long-time dependence that arises in the memory functions for the generalized Langevin when only *linear* densities are included in the projection $\mathcal{P}$. In the theory of liquids, the Laplace transform of these memory functions are generalized transport coefficients, which reduce to the Green-Kubo expressions in the limit of small z and k. Equation (34) can be cast in the form in which the full generalized transport coefficients are expressed as a sum of bare transport coefficients and the $\Sigma_{11}(z)$ terms, which renormalize the bare coefficients and account for the complicated memory effects observed in dense liquids [46]. In the limit in which the energy density is neglected in the basis set and only bilinear modes are included in the multilinear basis set, the idealized and extended mode-coupling theory models [53] of the glass transition can be obtained [46,54].

Finally, we mention that in Ref. [46] it was shown that by rearranging the terms, along the lines of Sec. II D, $\hat{G}_{\alpha\alpha'}$ in the Θ_i can be replaced by the real diagonal in wave vector $G_{\alpha\alpha'}$, with the restriction in summations over α, β, etc., that none of their wave-vector sets are identical. This diagonal $G_{\alpha\alpha'}$ will factor again as in Eq. (25). Then, Eq. (34), Eq. (33), and Eq. (25) lead to a self-consistent equation for G_{11}.

III. MULTIPLE-TIME CORRELATIONS

A. Separating slow and fast behavior in the context of multiple times

We now turn to multiple-time correlation functions like $\langle Q(t_2+t_1)Q(t_1)Q\rangle$. At first glance, it appears attractive to use the formal solution of Eq. (9),

$$Q_\alpha(t)=G_{\alpha\delta}(t)Q_\delta(0)+\int_0^t G_{\alpha b}(t-\tau)\phi_\delta(\tau)d\tau, \tag{35}$$

to get an explicit expression for $\langle Q_\alpha(t_1+t_2)Q_\beta(t_1)Q_\gamma^*\rangle$. After all, inserting Eq. (35) yields

$$\begin{aligned}\langle Q_\alpha(t_1+t_2)Q_\beta(t_1)Q_\gamma^*\rangle=&\int_0^{t_1+t_2}d\tau_2\int_0^{t_1}d\tau_1\\&\times G_{\alpha\eta}(t_1+t_2-\tau_2)G_{\beta\delta}(t_1-\tau_1)\\&\times[\langle Q_\eta Q_\delta Q_\gamma^*\rangle 4\delta(\tau_2)\delta(\tau_1)\\&+\langle\phi_\eta(\tau_2)\phi_\delta(\tau_1)Q_\gamma^*\rangle].\end{aligned} \tag{36}$$

It is tempting to assume that the expression in Eq. (36) involving the fluctuating force behaves as $\delta(\tau_2)\delta(\tau_1)$ at long times in an analogous fashion to Eq. (12), leading directly to a local equation in time,

$$\langle Q_\alpha(t_1+t_2)Q_\beta(t_1)Q_\gamma^*\rangle\overset{?}{=}G_{\alpha\eta}(t_1+t_2)G_{\beta\delta}(t_1)\tilde{M}_{\eta\delta\gamma}, \tag{37}$$

where $\tilde{M}_{\eta\delta\gamma}$ is related to the infinite time integral of $[\langle Q_\eta Q_\delta Q_\gamma^*\rangle 4\delta(\tau_2)\delta(\tau_1)+\langle\phi_\eta(\tau_2)\phi_\delta(\tau_1)Q_\gamma^*\rangle]$. However, things are not this simple as can be seen by using time translation invariance to write $\langle Q_\alpha(t_1+t_2)Q_\beta(t_1)Q_\gamma^*\rangle=\langle Q_\alpha(t_2)Q_\beta Q_\gamma^*(-t_1)\rangle$. Applying again Eq. (35), we obtain

$$\begin{aligned}\langle Q_\alpha(t_2)Q_\beta Q_\gamma^*(-t_1)\rangle=&\int_0^{t_2}d\tau_2\int_0^{-t_1}d\tau_1\\&\times G_{\alpha\eta}(t_1+t_2-\tau_2)G_{\gamma\delta}^*(-t_1-\tau_1)\\&\times[\langle Q_\eta Q_\beta Q_\delta^*\rangle 4\delta(\tau_2)\delta(\tau_1)\\&+\langle\phi_\eta(\tau_2)Q_\beta\phi_\delta^*(\tau_1)\rangle],\end{aligned}$$

of which the local time version would be

$$\langle Q_\alpha(t_2)Q_\beta Q_{\hat\gamma}^*(-t_1)\rangle K_{\hat\gamma\gamma}^{-1}\overset{?}{=}G_{\alpha\eta}(t_2)\bar{M}_{\eta\beta\delta}G_{\delta\gamma}(t_1), \tag{38}$$

where we have used the time-translation property, $G_{\alpha\hat\beta}(t)K_{\hat\beta\beta}=G_{\beta\hat\alpha}^*(-t)K_{\hat\alpha\alpha}$ (see Appendix B), and defined

$$\begin{aligned}\bar{M}_{\delta\beta\theta}=\Bigg\{&-\int_0^\infty\int_0^\infty\langle\phi_\delta(\tau_2)Q_\beta\phi_{\hat\theta}^*(-\tau_1)\rangle d\tau_1 d\tau_2\\&+\langle Q_\delta Q_\beta Q_{\hat\theta}^*\rangle\Bigg\}K_{\hat\theta\theta}^{-1}.\end{aligned} \tag{39}$$

Clearly, Eqs. (38) and (37) are in contradiction since, in general, they will have different time behavior.

The question of which (if either) instantaneous form is approximately correct can be resolved by noting that products of the fluctuating force $\phi(\tau)$ cannot always be treated as "fast," nor as Gaussian random variables. This observation has been noted previously by Schramm and Oppenheim [45] who considered the quantity $\langle\phi(\tau_1)\phi(\tau_2)\phi(\tau_3)\rangle$ and showed that it does not have a purely fast decay. To understand this point, consider the *equal* time correlation function $\langle Q_\alpha(t)Q_\beta(t)Q_\gamma(t)\rangle=\langle Q_\alpha Q_\beta Q_\gamma\rangle$. Inserting Eq. (35), taking the limit $t\to\infty$, and noting that in that limit $G(t)\to 0$, one obtains

$$\begin{aligned}\langle Q_\alpha Q_\beta Q_\gamma\rangle=\lim_{t\to\infty}&\int_0^t\int_0^t\int_0^t G_{\alpha\eta}(t-\tau_1)G_{\beta\delta}(t-\tau_2)\\&\times G_{\gamma\zeta}(t-\tau_3)\langle\phi_\eta(\tau_1)\phi_\delta(\tau_2)\phi_\zeta(\tau_3)\rangle\\&\times d\tau_1 d\tau_2 d\tau_3.\end{aligned} \tag{40}$$

If $\phi(\tau)$ were Gaussian with zero mean, the three-point correlation on the right-hand side would be zero, but since the left-hand side of Eq. (40) does not vanish, $\phi(\tau)$ is not a Gaussian fluctuating force.

The three-point correlation function in Eq. (40) cannot have a purely fast decay either, since, by isotropy, $\langle\phi_\eta(\tau_1)\phi_\delta(\tau_2)\phi_\zeta(\tau_3)\rangle=O(k^4)$, whereas the left-hand side is $O(k^0)$. It therefore follows that upon integration of the slow part of $\langle\phi_\eta(\tau_1)\phi_\delta(\tau_2)\phi_\zeta(\tau_3)\rangle$, one needs to generate a factor k^{-4}. Schramm and Oppenheim obtained the explicit form of the slow behavior of the three-time correlation function of the fluctuating force for the case of a single slow variable *A*. It was shown that for τ_2, $\tau_3>\tau_1$, and small $|\mathbf{k}_1|$ (other cases are similar),

$$\begin{aligned}\langle\phi_{\mathbf{k}_1}(\tau_1)\phi_{\mathbf{k}_2}(\tau_2)\phi_{\mathbf{k}_3}(\tau_3)\rangle\approx&\,2|\mathbf{k}_1|^2D\exp[D|\mathbf{k}_1|^2|\tau_2-\tau_1|]\\&\times\langle\hat{A}_{\mathbf{k}_1}\phi_{\mathbf{k}_2}(\tau_2-\tau_3)\phi_{\mathbf{k}_3}\rangle,\end{aligned}$$

where D is the diffusion constant, which is clearly a slowly decaying function of $\tau_2-\tau_1$. On the other hand, it appears that there is a fast decay in $\tau_2-\tau_3$, so that the whole expression is small when that time difference becomes large. Nonetheless, the slow behavior in $\tau_2-\tau_1$ will bring about a factor of $O(1/k^2)$ upon integration. For the full restoration of the $O(k^0)$ term on the left-hand side of Eq. (40), we refer the reader to the original paper [45].

Apparently, the assumption that $\mathcal{P}$ projects out all the slow behavior is not sufficient to specify when a correlation function is fast decaying since clearly $\phi_\alpha(t)$ itself is not a fast variable in every context. Notice that despite the appearance of slow behavior in the correlation function

$\langle \phi_{\mathbf{k}_1}(\tau_1)\phi_{\mathbf{k}_2}(\tau_2)\phi_{\mathbf{k}_3}(\tau_3)\rangle$, there are instances in which a multiple-time correlation function of fluctuating forces is certainly small; namely, when at least two of the time arguments of the forces are well separated. If the time arguments of the fluctuating forces are not well separated, slow behavior can occur. In Eq. (36), we cannot assume that the integrand is peaked around $(\tau_2,\tau_1)=(0{,}0)$ because these two variables can come arbitrarily close in the integration over τ_2 and τ_1 along the line $\tau_1 \approx \tau_2$ and slow behavior can be expected. We conclude that the local time dependence of the instantaneous Eq. (37) cannot be justified.

We propose the following general rule to determine when a correlation function is fast decaying: *In a correlation function involving fluctuating forces, the function decays quickly in a pair of time arguments, provided these are well separated in time*. Note that ''well separated'' here means that the time difference is larger than the microscopic time τ_m. In applying this rule to situations when integrations are carried out over the time arguments of fluctuating forces, we require that the time arguments can only get close at isolated points, which give contributions of measure zero to the integral.

With these rules in mind, consider the correlation function

$$\langle \phi_\alpha(-\tau_2)\phi_\beta\phi_\gamma(\tau_1)\rangle.$$

This is clearly fast in τ_2 as well as in τ_1 provided τ_2 and τ_1 are positive. Therefore, Eq. (38) should be correct, as the correlations of the fluctuating forces in Eq. (39) are of the form above, which we can write as

$$\langle \phi_\alpha(-\tau_2)\phi_\beta\phi_\gamma(\tau_1)\rangle = \langle \dot{Q}_\alpha e^{\mathcal{L}_\perp \tau_2}\mathcal{P}_\perp \phi_\beta e^{\mathcal{L}_\perp \tau_1}\mathcal{P}_\perp \dot{Q}\rangle.$$

We observe that the correlation function above is fast in τ_1 and τ_2 provided $\tau_1 \gg \tau_m$ and $\tau_2 \gg \tau_m$ since it has the form of a succession of two fast forward propagations, which yields an expression in which all time arguments are well separated. If one of the times were negative, i.e., one of the propagators propagated backward in time, the expression would no longer be (purely) fast. Hence an alternative way of identifying terms that are fast in all time arguments is to require that they have only forward fast propagation when applied in succession.

B. Correlation functions involving multiple times

Using the conclusions of the preceding section, we will now derive a recursion relation for multiple-time correlation functions. We consider the general case, denoted by $G^{(n)}_{\alpha_n,\alpha_{n-1},\ldots,\alpha_0}(t_n,t_{n-1},\ldots,t_1)$ or $G^{(n)}_{\{\alpha_i\}}(\{t_i\})$, defined as

$$G^{(n)}_{\{\alpha_i\}}(\{t_i\}) = \langle Q^*_{\hat{\alpha}_0} Q_{\alpha_n}(t_1+\cdots+t_n)\cdots Q_{\alpha_1}(t_1)\rangle K^{-1}_{\hat{\alpha}_0\alpha_0},$$

with $i=1,\ldots,n$ and $t_i \geqslant 0$ so the arguments are time ordered. We write

$$\begin{aligned}
&\langle Q^*_{\hat{\alpha}_0} Q_{\alpha_n}(t_1+t_2+\cdots+t_n)\cdots Q_{\alpha_2}(t_1+t_2)Q_{\alpha_1}(t_1)\rangle\\
&\quad = \langle Q^*_{\hat{\alpha}_0} e^{\mathcal{L}t_1} Q_{\alpha_1} e^{\mathcal{L}t_2} Q_{\alpha_2}\cdots e^{\mathcal{L}t_{n-1}} Q_{\alpha_{n-1}} e^{\mathcal{L}t_n} Q_{\alpha_n}\rangle\\
&\quad \equiv \langle X e^{\mathcal{L}t_{n-1}} B\rangle,
\end{aligned}$$

where $B = Q_{\alpha_{n-1}} Q_{\alpha_n}(t_n)$ and X is the operator

$$X = Q^*_{\hat{\alpha}_0} e^{\mathcal{L}t_1} Q_{\alpha_1} e^{\mathcal{L}t_2} Q_{\alpha_2}\cdots e^{\mathcal{L}t_{n-1}}.$$

Using Eq. (8) applied to B, and inserting the result into $\langle X e^{\mathcal{L}t_{n-1}} B\rangle$, we get

$$\begin{aligned}
\langle X e^{\mathcal{L}t_{n-1}} B\rangle &= \langle Q^*_{\delta} B\rangle K^{-1}_{\delta\hat{\delta}} \langle X Q_{\hat{\delta}}(t_{n-1})\rangle\\
&\quad - \int_0^{t_{n-1}} \langle \dot{Q}^*_{\delta} e^{\mathcal{L}_\perp \tau_1}\mathcal{P}_\perp B\rangle K^{-1}_{\delta\hat{\delta}}\\
&\quad \times \langle X Q_{\hat{\delta}}(t_{n-1}-\tau_1)\rangle d\tau_1 + \langle X e^{\mathcal{L}_\perp t_{n-1}}\mathcal{P}_\perp B\rangle.
\end{aligned} \tag{41}$$

From the discussion in Sec. III A, it is now apparent that the third term can be considered fast in t_{n-1} because only forward propagation occurs in X since all t_i are positive, and there is a projected propagation in t_{n-1}. For macroscopic times for which $t_{n-1} \gg \tau_m$, this term can be neglected. Note, however, this term could not be neglected in integrals of Eq. (41) over the time t_{n-1}. Inserting $B = Q_{\alpha_{n-1}} Q_{\alpha_n}(t_n)$ and using Eq. (35), one obtains

$$\begin{aligned}
G^{(n)}_{\{\alpha_i\}}(\{t_i\}) &= \int_0^{t_{n-1}}\int_0^{t_n} G_{\alpha_n\beta}(t_n-\tau) M_{\beta\alpha_{n-1}\delta}(\tau,\tau_1)\\
&\quad \times G^{(n-1)}_{\delta,\alpha_{n-2}\ldots}(t_{n-1}-\tau_1, t_{n-2},\ldots)\, d\tau\, d\tau_1\\
&\quad + \text{fast term in } t_{n-1},
\end{aligned} \tag{42}$$

where

$$\begin{aligned}
M_{\beta\alpha\delta}(\tau,\tau_1) &= [4\langle Q_\beta Q_\alpha Q_{\hat{\delta}}\rangle \delta(\tau)\delta(\tau_1)\\
&\quad - \langle \dot{Q}^*_{\hat{\delta}} e^{\mathcal{L}_\perp \tau_1}\mathcal{P}_\perp \phi_\beta(\tau) Q_\alpha\rangle] K^{-1}_{\hat{\delta}\delta}.
\end{aligned} \tag{43}$$

Equation (42) is the desired recursion relation. Neglecting the term that is fast in t_{n-1}, the n multiple-time correlation functions can be related to the $n-1$ multiple-time correlation, and thus ultimately in terms of $G^{(1)}_{\alpha_1\alpha_0}(t_1) = G_{\alpha_1\alpha_0}(t_1)$. The instantaneous version of Eq. (42) is simply

$$G^{(n)}_{\alpha_n,\ldots}(t_n,\ldots) = G_{\alpha_n\beta}(t_n)\overline{M}_{\beta\alpha_{n-1}\delta} G^{(n-1)}_{\delta,\alpha_{n-2},\ldots}(t_{n-1},\ldots), \tag{44}$$

where $\overline{M}_{\delta\alpha\theta} = \int_0^\infty d\tau_1 \int_0^\infty d\tau M_{\delta\alpha\theta}(\tau,\tau_1)$.

Applying Eq. (44) to the three-time correlation function $G_{\alpha\gamma\beta}(t_2,t_1)$, Eq. (38) is recovered,

$$G_{\alpha\gamma\beta}(t_2,t_1) = G_{\alpha\delta}(t_2)\overline{M}_{\delta\gamma\theta} G_{\theta\beta}(t_1). \tag{45}$$

Again using the recursion relation, one can also derive equations for correlation functions involving four or more times, e.g.,

$$G^{(3)}_{\alpha\beta\gamma\delta}(t_3,t_2,t_1)=G_{\alpha\zeta}(t_3)\overline{M}_{\zeta\beta\theta}G_{\theta\eta}(t_2)\overline{M}_{\eta\gamma\lambda}G_{\lambda\delta}(t_1). \tag{46}$$

It is clear now that any multiple-time correlation $G^{(n)}$ can be written as a product of n factors of G_{11} and $n-1$ vertices $\overline{M}$.

C. *N* ordering of triple-time correlation function

In this section, we consider the leading N-order and mode-coupling term expressions for the triple-time correlation function for linear densities in which $|\alpha|=|\beta|=|\gamma|=1$. Taking Eq. (45) for the linear densities, this correlation function is given by

$$G_{\alpha1\beta}(t_2,t_1)=G_{\alpha\delta}(t_2)\overline{M}_{\delta1\theta}G_{\theta\beta}(t_1). \tag{47}$$

From this relation, it is evident that the N ordering of $\overline{M}_{\gamma1\delta}$ follows from that of $G^{-1}_{\gamma\alpha}(t_2)G_{\alpha1\beta}(t_2,t_1)G^{-1}_{\beta\delta}(t_1)$, and hence we need to establish the N-ordering properties of $\langle Q_\alpha(t_2+t_1)Q_1(t_1)Q_\beta\rangle$. One can show, by induction in $|\beta|$, that

$$\langle Q_\alpha(t_2+t_1)Q_1(t_1)Q_\beta\rangle=\begin{cases} O(N^{|\alpha|+1}) & \text{if } |\alpha|<|\beta|,\\ O(N^{|\beta|}) & \text{if } |\alpha|=|\beta|,\\ O(N^{|\beta|+1}) & \text{if } |\alpha|>|\beta|.\end{cases}$$

Combining with Eqs. (42) and (20), we obtain

$$G_{\alpha1\beta}(t_2,t_1)=\begin{cases} 0(N^{1-(|\beta|-|\alpha|)}) & \text{if } |\alpha|<|\beta|,\\ O(N^{0}) & \text{if } |\alpha|=|\beta|,\\ O(N^{1}) & \text{if } |\alpha|>|\beta|.\end{cases} \tag{48}$$

Using Eqs. (21) and (48) to establish the N order of $G^{-1}_{\gamma\alpha}(t_2)G_{\alpha1\beta}(t_2,t_1)G^{-1}_{\beta\delta}(t_1)$, one finds that the N ordering of $\overline{M}_{\gamma1\delta}$ follows the same N-ordering rules as $G_{\gamma1\delta}(t_2,t_1)$.

With the N-ordering expressions above, the dominant contributions to $G_{111}(t_2,t_1)$ are given by

$$\begin{aligned}G_{111}(t_2,t_1)=G_{11}(t_2)*\overline{M}_{111}*G_{11}(t_1)&\\ +G_{12}(t_2)*\overline{M}_{211}*G_{11}(t_1)&\\ +G_{11}(t_2)*\overline{M}_{112}*G_{21}(t_1)+O(N^{-1}).&\end{aligned} \tag{49}$$

The leading mode-coupling corrections to Eq. (49) involve a large number of terms of order N^{-1}. Collecting these additional terms gives a net factor of $M\approx Vk_c^3$, so that the sum of all N^{-1} terms gives a term of order $M/N\approx(k_c\xi)^3$, which survives in the thermodynamic limit. To first order in M/N, one obtains the following correction terms:

$$\begin{aligned}&G_{13}(t_2)*\overline{M}_{312}*G_{21}(t_1)+G_{13}(t_2)*\overline{M}_{311}*G_{11}(t_1)\\ &\quad+G_{12}(t_2)*\overline{M}_{212}*G_{21}(t_1)+G_{12}(t_2)*\overline{M}_{213}*G_{31}(t_1)\\ &\quad+G_{11}(t_2)*\overline{M}_{113}*G_{31}(t_1),\end{aligned}$$

These results can be easily extended to higher-order correlations $G^{(n)}_{\{\alpha_i\}}$ with $n>3$ and where $|\alpha_i|=1$ since all the necessary N orderings are known. Thus, any multiple-time correlation function of Q_1's can be expressed in terms of the vertices $\overline{M}_{\alpha1\beta}$ and *two-time* (but possibly multiple-point) correlation functions. In turn, the multiple-point correlation functions can be expressed in terms of the vertices $\overline{M}_{\alpha\beta}$ and the linear propagator $G_{11}(t)$ as explained in Sec. II D, and hence all time dependences in multiple-time correlation functions at long times can be expressed in terms of the two-time correlation functions of linear densities. From the mode-coupling formalism, the two-time correlation functions can be evaluated self-consistently via the relations (34) and (33).

Using the results from Sec. II D, and Eqs. (49) and (30), one can obtain the leading N-order expressions for G_{111} in terms of $\overline{M}_{11}$, $\overline{M}_{111}$, and $G_{11}(t)$ as follows. Inserting the reduced forms of the vertices M_{211} and M_{112} that are derived in Appendix A into Eq. (49) yields

$$G^{111}_{\mathbf{k-q,q,k}}(t_2,t_1)=H_1+H_2+H_3, \tag{50}$$

where

$$\begin{aligned}H_1&=G^{11}_{\mathbf{k-q}}(t_2)\cdot\overline{M}^{111}_{\mathbf{k-q;q;k}}\cdot G^{11}_{\mathbf{k}}(t_1),\\ H_2&=G^{12}_{\mathbf{k-q;-q,k}}(t_2):[K^{11}_{\mathbf{q}}\circ G^{11}_{\mathbf{k}}(t_1)],\\ H_3&=G^{11}_{\mathbf{k-q}}(t_2)\cdot G^{21}_{\mathbf{k-q,q;k}}(t_1).\end{aligned}$$

In H_2, we can use Eq. (30) to express $G^{12}_{\mathbf{k-q;-q,k}}(t_2)$ in terms of the linear $G_{11}(t)$ and vertices $\overline{M}$. For G_{21} in H_3, using the fact that $G_{\alpha\beta}(t)=G_{\hat\beta\hat\alpha}(t)K_{\hat\alpha\alpha}K^{-1}_{\hat\beta\beta}$ [Eq. (B3)], an analogous expression for G_{21} is obtained,

$$G^{21}_{\mathbf{k-q,q;k}}(t_1)=S\int_0^{t_1}K^{-1}_{\mathbf{k}}\cdot G^{11}_{\mathbf{k}}(\tau_1)\cdot\overline{M}^{12}_{\mathbf{k;k-q,q}}:\{[G^{11}_{\mathbf{q}}(t_1-\tau_1)\cdot K_{\mathbf{q}}]\circ[G^{11}_{\mathbf{k-q}}(t_1-\tau_1)\cdot K_{\mathbf{k-q}}]\}d\tau_1.$$

Thus, in Eq. (50), we have

$$H_2=\int_0^{t_2}G^{11}_{\mathbf{k-q}}(\tau_2)\cdot\overline{M}^{12}_{\mathbf{k-q;-q,k}}:\{[G^{11}_{\mathbf{-q}}(t_2-\tau_2)\cdot K_{\mathbf{q}}]\circ[G^{11}_{\mathbf{k}}(t_2-\tau_2)\cdot G^{11}_{\mathbf{k}}(t_1)]\}d\tau_2, \tag{51}$$

$$H_3 = S\int_0^{t_1} K_{\mathbf{k}}^{-1}\cdot G_{\mathbf{k}}^{11}(\tau_1)\cdot \overline{M}_{\mathbf{k};\mathbf{k}-\mathbf{q},\mathbf{q}}^{12}:\{[G_{\mathbf{q}}^{11}(t_1-\tau_1)\cdot K_{\mathbf{q}}]\circ[G_{\mathbf{k}_1-\mathbf{k}_2}^{11}(t_1-\tau_1)\cdot G_{\mathbf{k}-\mathbf{q}}^{11}(t_2)\cdot K_{\mathbf{k}-\mathbf{q}}]\}d\tau_1 . \tag{52}$$

In a subsequent paper [55], we demonstrate that the expressions above give excellent results for a moderately dense hard-sphere system in the hydrodynamic regime.

IV. COMPARISON WITH KAWASAKI'S THEORY: NON-GAUSSIAN EFFECTS

Roughly 20 years ago, Ronis [41] examined higher-order correlation functions within the Kawasaki mode-coupling formalism [35,48]. The treatment itself is too technical to recapture here, so we will simply state the results from that paper to compare with those from the present theory. For a multiple point correlation, Ronis obtains [his Eq. (3.11)]

$$\begin{aligned} C_{k_0k_1k_2}^{\alpha_0\alpha_1\alpha_2}(t) &\equiv \langle\langle A_{\alpha_0,k_0}(t)A_{\beta_1,-k_1}A_{\beta_2,-k_2}\rangle\rangle \\ &\quad\times\langle A_{k_1}A_{k_1}^*\rangle_{\beta_1\alpha_1}^{-1}\langle A_{k_2}A_{k_2}^*\rangle_{\beta_2\alpha_2}^{-1} \\ &= 2\int_0^t dt_1 G_{\alpha_0\beta_0}(k_0,t-t_1)V_{k_0k_1k_2}^{\beta_0\beta_1\beta_2} \\ &\quad\times G_{\beta_1\alpha_1}(\mathbf{k}_1,t_1)G_{\beta_2\alpha_2}(\mathbf{k}_2,t_1). \end{aligned} \tag{53}$$

We keep Ronis's notation here, as it is close enough to ours to be understood. Equation (53) looks essentially like Eq. (30), but is missing the first term in Eq. (31) as might be expected from a Gaussian theory for three-point correlation functions. Intriguingly, this first term is all one would obtain for the three-point correlation function from a projection operator approach if only linear densities were included in the basis set for the long-time dynamics. In addition, the vertex V in the Gaussian theory also differs from the vertex M_{21} due to the subtraction terms in the basis set, which are not present. These differences in functional form of the vertices can significantly alter the time profile of both multiple-point and multiple-time correlation functions [55].

In Ref. [41], the following expression for a three-time correlation function was derived [Eq. (6.5b) therein]:

$$\begin{aligned} &\langle\langle A_{\alpha_0,k_0}(t_0)A_{\beta_1,k_1}^*(t_1)A_{\beta_2,k_2}^*(0)\rangle\rangle\langle A_{k_1}A_{k_1}^*\rangle_{\beta_1\alpha_1}^{-1} \\ &\quad= 2\int_0^{t_0} d\tau_1 G_{\alpha_0\beta_0}(k_0,t_0-\tau_1)V_{k_0,-k_1,k_2}^{\beta_0\beta_1\beta_2} \\ &\qquad\times G_{\beta_2\alpha_2}(k_2,\tau_1)\langle A_{\beta_1,k_1}(\tau_1)A_{\alpha_1,k_1}(t_1)\rangle \\ &\qquad+2\int_0^{t_1} d\tau_1 G_{\alpha_1\beta_0}(k_1,t_1-\tau_1)V_{k_1,-k_0,k_2}^{\beta_0\beta_1\beta_2}G_{\beta_2\alpha_2}(k_2,\tau_1) \\ &\qquad\times\langle A_{\beta_1,-k_0}(\tau_1)A_{\alpha_0,k_0}(t_0)\rangle. \end{aligned} \tag{54}$$

Comparison between Eq. (54) and the expression for the three-time correlation function in Eq. (50) is facilitated by noting that in the instantaneous approximation and neglecting mode-coupling corrections, we can write

$$G_{\mathbf{k}}^{11}(t_2-\tau_2)\cdot G_{\mathbf{k}}^{11}(t_1) = G_{\mathbf{k}}^{11}(t_1+t_2-\tau_2);$$

$$G_{\mathbf{k}-\mathbf{q}}^{11}(t_2)\cdot G_{\mathbf{k}-\mathbf{q}}^{11}(t_1-\tau_1) = G_{\mathbf{k}-\mathbf{q}}^{11}(t_1+t_2-\tau_1).$$

From careful inspection of Eqs. (54) and (50), one sees that H_3 [see Eq. (52)] is essentially equivalent to the second term in Eq. (54). However, the term H_2 differs from the first term in Eq. (54) in two ways. First, the way in which the indices are contracted with the vertex $V_{k_0,-k_1,k_2}^{\beta_0\beta_1\beta_2}$, as written in Ref. [41], differs from the tensor contractions in H_2. Second, and more importantly, there seem to be significant differences in the upper limits in the time-convolution integrals, which in Ref. [41] is $t_0=t_1+t_2$, as opposed to t_2. This is particularly intriguing in light of the observation that the upper limit of t_0 was obtained in Eq. (37) where the time dependence of the correlation function of the fluctuating forces was treated incorrectly. Nonetheless, in both mode-coupling theories, the higher-order time correlation functions are expressed in terms of ordinary (two-) time correlation functions. The major differences between the theories arise because of the Gaussian approximation in the Kawasaki formalism. Hence it is not surprising that some (static) three-point correlations are missed since they vanish if the linear densities Q_1 are assumed to obey Gaussian statistics at all times. This deficiency was noted by Ronis who suggested that these differences result in significant deviations only at short times. It is clear from the present formalism, however, that this is not the case since terms of the form $G_{11}(t_2)*\overline{M}_{111}*G_{11}(t_1)$ decay slowly in both t_1 and t_2. These findings have been confirmed in numerical simulations of hard-sphere systems [55].

V. HIGHER-ORDER CORRELATION FUNCTIONS FOR THE IDEAL GAS

In this section, the mode-coupling formalism will be illustrated for an ideal gas system in the grand-canonical ensemble composed of particles of mass m in a volume V at an inverse temperature β. In the ideal gas the motion of each particle j is given by

$$\mathbf{r}_j(t) = \mathbf{r}_j(0) + \frac{\mathbf{p}_j(0)}{m}t, \quad \mathbf{p}_j(t) = \mathbf{p}_j(0).$$

Given the simple form of the particles trajectories, any time correlation function can be calculated exactly and compared with the expressions that follow from mode-coupling theory.

A. Conserved quantities

An essential step in applying the formalism to a particular system is the identification of the slow variables of the system. In any gas composed of point particles, particle number, momentum, and energy are conserved and hence their corresponding densities are slowly varying quantities. The ideal gas system is quite different from simple gases in that it has many more conserved quantities since the momentum p_j of each particle is conserved along all directions. Consequently, a tagged particle density of the form $p_{jx}^{m_x}p_{jy}^{m_y}p_{jz}^{m_z}e^{i\mathbf{k}\cdot\mathbf{p}_j}$, where m_x, m_y, and m_z are arbitrary integers, should be included for each particle j in the set of slow variables. However, for collective modes, it is not hard to show that it suffices to include densities of all analytical functions of the momenta $f(\mathbf{p}_j)$, i.e.,

$$\sum_{j=1}^{N} f(\mathbf{p}_j)e^{i\mathbf{k}\cdot\mathbf{r}_j},$$

since the contribution of a single tagged particle to correlation of extensive variables is $O(1/N)$.

Taking the Hermite polynomials H_n as a basis for the functions $f(p)$, where

$$H_0(u)=1,\quad H_1(u)=2u;\quad H_n(u)=(-1)^n e^{u^2}\frac{d^n}{du^n}e^{-u^2},$$

the complete set of linear slow variables is given by

$$A_{\mathbf{k}}^{(i)}=\sum_{j=1}^{N}\frac{H_{i_x}(u_j^x)H_{i_y}(u_j^y)H_{i_z}(u_j^z)}{\sqrt{2^{i_x+i_y+i_z}i_x!\,i_y!\,i_z!}}e^{i\mathbf{k}\cdot\mathbf{r}_j},\tag{55}$$

where $\{i\}$ denotes the set of three indices $\{i_x,i_y,i_z\}$, each of which runs from zero to infinity. If we define $u_j^x=p_j^x\sqrt{\beta/2m}$, $u_j^y=p_j^y\sqrt{\beta/m}$, and $u_j^z=p_j^z\sqrt{\beta/m}$, then the inner product of the Hermite polynomials corresponds to the canonical average:

$$\int_{-\infty}^{\infty}H_n(u)H_m(u)\frac{e^{-u^2}}{\sqrt{\pi}}du=2^n n!\,\delta_{mn}=\langle H_n(u)H_m(u)\rangle.\tag{56}$$

Since $\langle H^i(u)\rangle=0$ unless $i=0$, $\hat{A}_{\mathbf{k}}^{\{i\}}$ is given by

$$\hat{A}_{\mathbf{k}}^{\{i\}}=A_{\mathbf{k}}^{\{i\}}-\langle N\rangle\delta_{i_z0}\delta_{i_y0}\delta_{i_z0}\delta_{\mathbf{k}0}$$

and the correlation function $\langle\hat{A}_{\mathbf{k}}^{\{i\}}\hat{A}_{\mathbf{k}}^{\{j\}*}\rangle$ is given by

$$\langle\hat{A}_{\mathbf{k}}^{\{i\}}\hat{A}_{\mathbf{k}}^{\{j\}*}\rangle=\langle N\rangle\delta_{i_xj_x}\delta_{i_yj_y}\delta_{i_xj_z}.$$

B. Two-time, two-point correlation functions

Consider the density mode N_k, which corresponds to $A_{\mathbf{k}}^{\{0\}}$ ($\{0\}$ is short for $\{0, 0, 0\}$). For $\mathbf{k}\neq 0$, the density-density time correlation function is given by

$$G_{\mathbf{k}}^{\{0\}\{0\}}(t)=\frac{\left\langle\sum_{j=1}^{N}\sum_{l=1}^{N}\exp\{i\mathbf{k}\cdot[\mathbf{r}_j(t)-\mathbf{r}_l]\}\right\rangle}{\langle N\rangle}=\langle e^{i\mathbf{k}\cdot\mathbf{p}_1t/m}\rangle.$$

This result follows from the fact that $\langle\Sigma_{i=1}^{N}\exp(\mathbf{r}_i\cdot\mathbf{k})\rangle=\langle N\rangle\delta_{\mathbf{k}0}$ and the statistical independence of particles. As the momentum $\mathbf{p}_1$ is Gaussian distributed, one obtains

$$\begin{aligned}G_{\mathbf{k}}^{\{0\}\{0\}}(t)&=\int_{-\infty}^{\infty}\frac{e^{i|\mathbf{k}|pt/m}e^{-\beta p^2/(2m)}}{\sqrt{2\pi m/\beta}}dp=\exp[-|\mathbf{k}|^2t^2/2m\beta]\\&=e^{-(\tilde{k}t)^2/2},\end{aligned}\tag{57}$$

where $\tilde{k}=|\mathbf{k}|/\sqrt{m\beta}$ is a conveniently scaled wave vector.

We will compare the exact result Eq. (57) to the result from the mode-coupling framework of this paper obtained using Eqs. (9) and (10). The first point to note is that $\dot{Q}_\alpha(t)$ is proportional to Q_α, which follows from the facts the all Hermite polynomials have been included in the set of slow variables and that $(d/dt)H_n(u)=0$ for all n. This, in turn, implies that $\mathcal{P}_\perp\dot{Q}_\alpha=0$, and hence the fluctuating force $\phi_\alpha(t)$ vanishes for all t. According to Eqs. (10) and (14), $M_{\alpha\beta}(\tau)=2\delta(\tau)\overline{M}_{\alpha\beta}$, since $\phi_\alpha(t)=0$. Thus Eq. (13) is exact, with

$$\overline{M}_{\alpha\beta}=\langle\dot{Q}_\alpha Q_{\hat{\beta}}^*\rangle*K_{\hat{\beta}\beta}^{-1}.\tag{58}$$

Since $\dot{Q}_1$ is can be written as a linear combination of Q_1's, and, in general, $\dot{Q}_\alpha=\Sigma_{|\beta|\leqslant|\alpha|}a_{\alpha\beta}Q_\beta$, we conclude that $\langle\dot{Q}_\alpha Q_\beta^*\rangle=0$ for $\beta>\alpha$ since the multilinear basis set is orthogonal in mode order by construction. Similarly, since $\langle\dot{Q}_\alpha Q_\beta\rangle=-\langle Q_\alpha\dot{Q}_\beta^*\rangle$, $\langle\dot{Q}_\alpha Q_\beta\rangle=0$ for $\alpha>\beta$ and hence $\overline{M}_{\alpha\beta}$ is diagonal in mode order, implying that Eq. (13) decouples at each mode order n into equations for the multiple-point correlation functions $G_{nn}(t)$.

Focusing on the linear variables, Eq. (13) reduces to

$$\dot{G}_{\mathbf{k}}^{\{i\}\{j\}}(t)=\sum_{\{l\}}\overline{M}_{\mathbf{k}}^{\{i\}\{l\}}G_{\mathbf{k}}^{\{l\}\{j\}}(t).$$

Due to the orthogonality of the $A_{\mathbf{k}}^{\{i\}}$'s, $G_{\mathbf{k}}^{\{i\}\{j\}}(0)=\delta_{\{i\}\{j\}}$, and hence,

$$G_{\mathbf{k}}^{\{i\}\{j\}}(t)=[\exp(\overline{M}_{\mathbf{k}}^{11}t)]_{\{i\}\{j\}}.\tag{59}$$

The structure of the matrix $\overline{M}_{11}$ is relatively simple, which makes it possible to actually calculate $G_{11}(t)$ from Eq. (59). Fixing the direction of $\mathbf{k}$ to be along $\hat{x}$, for $|\mathbf{k}|\neq 0$ we note that

$$\dot{A}_{\mathbf{k}}^{\{j\}}=i\tilde{k}[\sqrt{j_x+1}\hat{A}_{\mathbf{k}}^{\{j_x+1,j_y,j_z\}}+\sqrt{j_z}\hat{A}_{\mathbf{k}}^{\{j_x-1,j_y,j_z\}}],$$

where Eqs. (55) and the recursion relation for the Hermite polynomials

$$2uH_{n-1}-2(n-1)H_{n-2}=H_n(u)$$

have been used. With Eq. (58), this leads to the tridiagonal form for the matrix $\overline{M}_{11}$ at linear order,

$$\bar{M}_{\mathbf{k}}^{\{i\}\{j\}}=i\tilde{k}\delta_{i_y j_y}\delta_{i_z j_z}(\sqrt{i_x+1}\,\delta_{i_x+1 j_x}+\sqrt{i_x}\,\delta_{i_x-1,j_x}). \quad (60)$$

The terms in Eq. (60) can be conveniently expressed as the expectation values of the raising and lowering operators in the Hermite basis representation of the quantum harmonic oscillator. Identifying

$$|n\rangle=\hat{A}_{\mathbf{k}}^{\{n,j_y,j_z\}}$$

and defining

$$\langle m|\mathcal{B}n\rangle\equiv\langle\hat{A}_{\mathbf{k}}^{\{m,j_y,j_z\}*}\mathcal{B}\hat{A}_{\mathbf{k}}^{\{n,j_y,j_z\}}\rangle/\langle N\rangle$$

for any operator $\mathcal{B}$ and

$$a|n\rangle=\sqrt{n}|n-1\rangle, \quad a^{\dagger}|n\rangle=\sqrt{n+1}|n+1\rangle,$$

one has

$$\langle m|an\rangle=\sqrt{n}\,\delta_{m,n-1}, \quad \langle m|a^{\dagger}n\rangle=\sqrt{n+1}\,\delta_{m,n+1}.$$

In this representation, the matrix $\bar{M}_{\mathbf{k}}^{\{i\}\{j\}}$ can be written as

$$\bar{M}_{\mathbf{k}}^{\{i\}\{j\}}=\langle j_x|\bar{\mathcal{M}}i_x\rangle,$$

where $\mathcal{M}$ is the operator

$$\bar{\mathcal{M}}=i\bar{k}(a^{\dagger}+a). \quad (61)$$

In essence, $\bar{\mathcal{M}}$ is nothing but the Liouville operator $\mathcal{L}$, restricted to act on the space of phase space functions that are linear combinations of $\hat{A}_{\mathbf{k}}$.

To reproduce Eq. (57), according to Eq. (59), we must evaluate

$$\langle 0|e^{\bar{\mathcal{M}}t}0\rangle,$$

which can be done in a straightforward fashion using the Baker-Campbell-Hausdorf formula [56]. This formula states that if $\mathcal{A}$ and $\mathcal{B}$ are linear operators, a linear operator $\mathcal{C}$ exists such that $e^{\mathcal{A}}e^{\mathcal{B}}=e^{\mathcal{C}}$, where $\mathcal{C}$ of the form $\mathcal{C}=\mathcal{A}+\mathcal{B}+\frac{1}{2}[\mathcal{A},\mathcal{B}]$ plus repeated commutators. Taking $\mathcal{A}=i\tilde{k}ta^{\dagger}$ and $\mathcal{B}=i\tilde{k}ta$ and noting that $[a,a^{\dagger}]=1$, Eq. (61) yields

$$e^{i\tilde{k}ta^{\dagger}}e^{i\tilde{k}ta}=e^{\bar{\mathcal{M}}t}e^{(\tilde{k}t)^2/2},$$

which can be rearranged to give

$$e^{\bar{\mathcal{M}}t}=e^{i\tilde{k}ta^{\dagger}}e^{i\tilde{k}ta}e^{-(\tilde{k}t)^2/2}, \quad (62)$$

and therefore

$$\langle 0|e^{\bar{\mathcal{M}}t}0\rangle=\langle e^{-i\tilde{k}ta}0|e^{i\tilde{k}ta}0\rangle e^{-(\tilde{k}t)^2/2}.$$

But as $e^{i\tilde{k}ta}|0\rangle=|0\rangle$,

$$\langle 0|e^{\bar{\mathcal{M}}t}0\rangle=e^{-(\tilde{k}t)^2/2},$$

which coincides, as expected, with the exact result (57).

The time correlations for other basis functions are now easily obtained using Eq. (62). For example,

$$\frac{\langle A_{\mathbf{k}}^{\{j\}}(t)A_{\mathbf{k}}^{\{0,0,0\}*}\rangle}{\langle N\rangle}=\langle 0|e^{i\tilde{k}ta}j_x\rangle e^{-(\tilde{k}t)^2/2}\delta_{j_y0}\delta_{j_z0}$$

$$=\frac{(it\tilde{k})^{j_x}}{\sqrt{j_x!}}e^{-(\tilde{k}t)^2/2}\delta_{j_y0}\delta_{j_z0}. \quad (63)$$

Note that it is only with an infinite set of conserved quantities that it is possible for a system with no dissipative terms to lead to relaxation. One might argue that taking a finite number of slow variables (say, mass, momentum, and energy density), the dissipative terms in $\bar{M}$ would no longer be zero. While this is correct and $\bar{M}$ is not purely imaginary, $\bar{M}$ would still be finite in each mode block, and one would get exponential decay in the instantaneous limit instead of Gaussian decay for all correlation functions.

C. Two-time, multiple-point correlation functions

Consider the correlation function

$$C_{\mathbf{k}-\mathbf{q},\mathbf{q};\mathbf{k}}^{\{0\}\{0\}\{0\}}(t)\equiv\langle\hat{N}_{\mathbf{k}-\mathbf{q}}(t)\hat{N}_{\mathbf{q}}(t)\hat{N}_{\mathbf{k}}^{*}\rangle/\langle N\rangle$$

with $|\mathbf{k}|\neq 0$, $|\mathbf{q}|\neq 0$, and $\mathbf{k}\neq q$. The direct calculation of this correlation function is simple if one notes that

$$\left\langle\sum_{l=1}^{N}e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_l(t)}\sum_{m=1}^{N}e^{i\mathbf{q}\cdot\mathbf{r}_m(t)}\sum_{n=1}^{N}e^{-i\mathbf{k}\cdot\mathbf{r}_n}\right\rangle\Big/\langle N\rangle$$

$$=\left\langle\sum_{l=1}^{N}\exp[i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_l(t)]e^{i\mathbf{q}\cdot\mathbf{r}_l(t)}e^{-i\mathbf{k}\cdot\mathbf{r}_l}\right\rangle,$$

since any term in the summation over particle indices in which $i\neq m$, $l\neq n$, or $m\neq n$ yields a Kronecker delta for one of the wave vectors. Such terms do not give a contribution if all wave vectors are nonzero. The wave vector $\mathbf{q}$ drops out of the expression and

$$C_{\mathbf{k}-\mathbf{q},\mathbf{q};\mathbf{k}}^{\{0\}\{0\}\{0\}}(t)=\left\langle\sum_{l=1}^{N}e^{i\mathbf{k}\cdot\mathbf{p}_l t/m}\right\rangle\Big/\langle N\rangle=G_{\mathbf{k}}^{\{0\}\{0\}}(t)=e^{-(\tilde{k}t)^2/2}. \quad (64)$$

The mode-coupling derivation of this same result goes as follows. From Eq. (30), noticing that $M_{21}=0$, we immediately obtain $G_{21}(t)=0$. The simplest argument for the vanishing of $G_{21}(t)$ is that since $\bar{M}$ is diagonal in mode order, no correlations between different mode orders exist, so that

$$G_{\alpha\beta}(t)=0 \quad \text{if } |\alpha|\neq|\beta|.$$

From the definition of the multilinear basis set in Eq. (5), $C_{\mathbf{k}-\mathbf{q};\mathbf{q};\mathbf{k}}^{\{0\}\{0\}\{0\}}(t)$ can be written in terms of the linear and bilinear densities as

$$C_{\mathbf{k}-\mathbf{q},\mathbf{q};\mathbf{k}}^{\{0\}\{0\}\{0\}}(t)=\langle Q_{\mathbf{k}-\mathbf{q},\mathbf{q}}^{\{0\}\{0\}}(t)\hat{N}_{\mathbf{k}}^{*}\rangle/\langle N\rangle+\langle\hat{N}_{\mathbf{k}-\mathbf{q}}\hat{N}_{\mathbf{q}}\hat{N}_{\mathbf{k}}^{*}\rangle$$

$$\times\langle\hat{N}_{\mathbf{k}}(t)\hat{N}_{\mathbf{k}}^{*}\rangle/\langle N\rangle^2.$$

However, since $G_{21}(t)=0$, $C^{\{0\}\{0\}\{0\}}_{\mathbf{k}-\mathbf{q},\mathbf{q};\mathbf{k}}(t)$ gets its value solely from the subtraction terms. Furthermore, since $\langle \hat{N}_{\mathbf{k}-\mathbf{q}}\hat{N}_{\mathbf{q}}\hat{N}^{*}_{\mathbf{k}}\rangle=\langle N\rangle$ for an ideal gas system, one gets

$$C^{\{0\}\{0\}\{0\}}_{\mathbf{k}-\mathbf{q},\mathbf{q};\mathbf{k}}(t)=\langle \hat{N}_{\mathbf{k}}(t)\hat{N}^{*}_{\mathbf{k}}\rangle/\langle N\rangle$$

in agreement with Eq. (64).

D. Multiple-time correlation functions

Finally, we conclude our discussion of the higher-order correlation functions in the ideal gas by examining the validity of the expressions for the multiple-time correlation functions in Eq. (45). For the three-time correlation function for the density mode N_k, direct calculation gives

$$\begin{aligned} G^{\{0\}\{0\}\{0\}}_{\mathbf{k}-\mathbf{q},\mathbf{q},\mathbf{k}}(t_2,t_1)&=\left\langle \sum_{l=1}^{N} \exp\{ip_l\cdot|\mathbf{k}(t_1+t_2)-\mathbf{q}t_2|\}\right\rangle \Big/ \langle N\rangle \\ &=\exp[-|\tilde{\mathbf{k}}(t_1+t_2)-\tilde{\mathbf{q}}t_2|^2/2], \qquad (65) \end{aligned}$$

where $\tilde{\mathbf{k}}=\mathbf{k}/\sqrt{m\beta}$ and $\tilde{\mathbf{q}}=\mathbf{q}/\sqrt{m\beta}$.

If $\mathbf{k}$ and $\mathbf{q}$ are both along $\hat{x}$, the mode-coupling expression for the multiple-time correlation [see Eq. (45)] is

$$G^{\{0\}\{0\}\{0\}}_{\mathbf{k}-\mathbf{q},\mathbf{q},\mathbf{k}}(t_2,t_1)=G^{\{0\}\{j\}}_{\mathbf{k}-\mathbf{q}}(t_2)\overline{M}^{\{j\}\{0\}\{i\}}_{\mathbf{k}-\mathbf{q},\mathbf{q},\mathbf{k}}G^{\{i\}\{0\}}_{\mathbf{k}}(t_1),$$

where the repeated sets of indices $\{i\}$ and $\{j\}$ are summed. Since $G^{\{i\}N}(t)$ was previously evaluated in Eq. (63), and $G^{\{i\}N}(t)=G^{N\{i\}*}(-t)$, the only unknown quantity in this expression is

$$\overline{M}^{\{j\}\{0\}\{i\}}_{\mathbf{k}-\mathbf{q},\mathbf{q},\mathbf{k}}=\langle \hat{A}^{\{j\}}_{\mathbf{k}-\mathbf{q}}\hat{A}^{\{0\}}_{\mathbf{q}}\hat{A}^{\{i\}*}_{\mathbf{k}}\rangle/\langle N\rangle.$$

Writing this out using Eq. (55), the only surviving terms in the summations over particle index for an ideal gas system are the terms where all indices are equal, so that

$$\overline{M}^{\{j\}\{0\}\{i\}}_{\mathbf{k}-\mathbf{q},\mathbf{q},\mathbf{k}}=\delta_{\{i\}\{j\}}\,.$$

Hence,

$$\begin{aligned} G^{\{0\}\{0\}\{0\}}_{\mathbf{k}-\mathbf{q},\mathbf{q},\mathbf{k}}(t_2,t_1)=\sum_{j_x=0}^{\infty} &\exp[-|\tilde{\mathbf{k}}-\tilde{\mathbf{q}}|^2t_2^2/2]e^{-|\tilde{\mathbf{k}}t_1|^2/2} \\ &\times\frac{1}{j_x!}[-t_1t_2\tilde{k}_x(\tilde{k}_x-\tilde{q}_x)]^{j_x}. \end{aligned}$$

This can be summed to

$$\exp\{-[|\tilde{\mathbf{k}}-\tilde{\mathbf{q}}|^2t_2^2-|\tilde{\mathbf{k}}|^2t_1^2-\tilde{k}_x(\tilde{k}_x-\tilde{q}_x)t_1t_2]/2\},$$

which corresponds to the exact result (65).

VI. SUMMARY

In this paper, a mode-coupling theory was presented in which multiple-point and multiple-time correlation functions are expressed in terms of ordinary two-point, two-time correlation functions and a set of vertices. The mode-coupling theory developed here does not assume that fluctuating forces (noise) are Gaussian distributed and therefore is a generalization of mode-coupling theories based on Kawasaki's formalism [35,48]. Furthermore, unlike kinetic theories, it is not restricted to low densities and should be applicable to dense fluids where cooperative motions of particles and collective modes are important.

The formalism is based on projection operator techniques, which, for ordinary two-point, two-time correlation functions, lead to a generalized Langevin equation in which the memory function decays on a microscopic time scale. The simple extension of the projection operator formalism to multiple-time correlation functions is complicated by the fact that the fluctuating forces appearing in the generalized Langevin equation do not obey Gaussian statistics. Furthermore, multiple-time correlations of the fluctuating force can in fact have a slow decay when the time arguments of these forces become comparable.

In order to treat multiple-time correlation functions of fluctuating forces properly, the correlation functions were massaged so that the time arguments of all fluctuating forces appearing in the correlations were guaranteed to be well separated, ensuring that all memory functions that arise in the mode-coupling theory decay to zero on a molecular time scale. This construction allows equations that are local in time to be obtained, which relate the multiple-time correlation function to two-time but multiple-point correlations coupled by essentially time-independent vertices. The multiple-point correlations, in turn, can be written as convolutions of two-point and two-time correlation functions coupled by time-independent vertices. These correlation functions can either be taken directly from experiment, simulation, or can be solved self-consistently within the mode-coupling formalism. The vertices, which are composed of a static part (Euler term) and a generalized transport coefficient, can similarly be calculated from kinetic theory or taken from molecular dynamics and Monte Carlo simulations.

The equations for higher-order correlation functions contain an infinite sum of terms that can be made tractable for systems with a finite correlation length by applying a cumulant expansion technique termed the *N*-ordering method. The method was applied to obtain the leading-order and first-order mode-coupling corrections of expressions for multiple-point and multiple-time correlation functions. A key step in the *N*-ordering method and the proper setup of the theory is the definition of an *orthogonal* multilinear basis. Although, in principle, it is possible to apply cumulant expansion methods to other choices of a multilinear basis, the orthogonalization procedure simplifies the perturbation analysis enormously and helps to avoid erroneous truncations of the mode-coupling series.

The expressions for the higher-order correlation functions bear a resemblance to those found by Ronis [41] within the framework of Kawasaki's mode-coupling theory. In this approach, the linear densities composing the set of slow variables are assumed to be Gaussian random variables at all times. Although the Gaussian assumption provides another method of simplifying the mode-coupling series for higher-order correlation functions, certain terms are absent from the Gaussian theory that are neither small nor quickly decaying.

The mode-coupling predictions for higher-order correlation functions for an ideal gas system were calculated analytically and shown to give the exact results for both multiple-time and multiple-point correlation functions. An essential step in arriving at the correct result was the inclusion of a complete set of densities in the set of slow variables. Although the ideal gas system does not constitute a rigorous test of the formalism since all fluctuating forces vanish, it is important to note that the formal mode-coupling theory expressions for the higher-order correlation functions yield the exact result. In a future paper [55], we compare the mode-coupling predictions for the multiple-point and multiple-time correlation functions for a hard-sphere fluid to data from simulations. The theoretical predictions of all higher-order correlation functions are in remarkable agreement with the simulation results in the hydrodynamic regime provided both Euler and dissipative vertex couplings are included.

The theory outlined here has obvious applications to multidimensional Raman and nuclear magnetic resonance spectroscopy, and simulation studies of dynamic heterogeneity in dense fluids, glasses, and polymers. Since the theory involves physical correlation functions, it is well positioned to address fundamental issues in characterizing the dynamics in systems exhibiting nonexponential relaxation processes and frustration. In fact the current formalism has been used in Refs. [46], [54] to justify some of the approximations made in mode-coupling theory for the supercooled liquids [53]. These avenues are currently being investigated.

ACKNOWLEDGMENTS

The authors would like to thank Irwin Oppenheim and David Reichman for useful discussions. This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

APPENDIX A: REDUCTION OF THE VERTICES $\bar{M}_{211}$ AND $\bar{M}_{112}$

Neglecting mode-coupling corrections, the vertices $\bar{M}_{211}$ and $\bar{M}_{112}$ can be reduced to very simple forms. The strategy used to simplify these terms is similar to that used for the factorization of $\bar{M}_{\alpha\beta}$ in Ref. [46]. First $\bar{M}_{112}$ is rewritten with the help of Eq. (45) as

$$\bar{M}_{112}=G_{1\alpha}^{-1}(t_2)G_{\alpha 1\beta}(t_2,t_1)G_{\beta 2}^{-1}(t_1).$$

Using the N ordering of $G_{\alpha 1\beta}(t_2,t_1)$, $G_{1\alpha}(t_2)$, and $G_{\beta 2}(t_1)$, one sees that to leading N order,

$$\bar{M}_{112}=G_{11}^{-1}(t_2)G_{112}(t_2,t_1)G_{22}^{-1}(t_1). \tag{A1}$$

In this expression, the leading N-order contributions are obtained from the part of the various factors in Eq. (A1) that are diagonal in the wave vector.

By the property in Eq. (19), G_{112} can be factored using

$$\begin{aligned}\langle\hat{A}^a_{\mathbf{k}-\mathbf{q}}(t_1+t_2)\hat{A}^b_{\mathbf{q}}(t_1)Q^{c,d*}_{\mathbf{k}-\mathbf{q}',\mathbf{q}'}\rangle\\ \approx\langle\hat{A}^a_{\mathbf{k}-\mathbf{q}}(t_1+t_2)\hat{A}^{c*}_{\mathbf{k}-\mathbf{q}}\rangle\langle\hat{A}^b_{\mathbf{q}}(t_1)\hat{A}^{d}_{\mathbf{q}}*\rangle\,\delta_{\mathbf{q}\mathbf{q}'}\\ +\langle\hat{A}^a_{\mathbf{k}-\mathbf{q}}(t_1+t_2)\hat{A}^d_{\mathbf{k}-\mathbf{q}}*\rangle\langle\hat{A}^b_{\mathbf{q}}(t_1)\hat{A}^c_{\mathbf{q}}*\rangle\,\delta_{\mathbf{k}-\mathbf{q},\mathbf{q}'}\,.\end{aligned}$$

In a similar fashion, K_{22}^{-1} factors to leading N order,

$$K^{22^{-1}}_{\mathbf{k}-\mathbf{q},\mathbf{q};\mathbf{k}-\mathbf{q}',\mathbf{q}'}\approx K^{-1}_{\mathbf{k}-\mathbf{q}}\circ K^{-1}_{\mathbf{q}}\,\delta_{\mathbf{q}\mathbf{q}'}+K^{-1}_{\mathbf{k}-\mathbf{q}}\bullet K^{-1}_{\mathbf{q}}\,\delta_{\mathbf{k}-\mathbf{q},\mathbf{q}'}\,.$$

This leads to the following factorization of the wave-vector-diagonal part of $G_{112}(t_2,t_1)$:

$$\begin{aligned}G^{112}_{\mathbf{k}-\mathbf{q};\mathbf{q};\mathbf{k}-\mathbf{q}',\mathbf{q}'}(t_2,t_1)\approx G^{11}_{\mathbf{k}-\mathbf{q}}(t_1+t_2)\circ G^{11}_{\mathbf{q}}(t_1)\,\delta_{\mathbf{q}\mathbf{q}'}\\ +G^{11}_{\mathbf{k}-\mathbf{q}}(t_1+t_2)\bullet G^{11}_{\mathbf{q}}(t_1)\,\delta_{\mathbf{k}\mathbf{q}-\mathbf{q}'}\,,\end{aligned}$$

where the notation introduced in Eq. (29) has been used.

The factorization of G_{22}^{-1} can be worked out as well,

$$\begin{aligned}G^{22^{-1}}_{\mathbf{k}-\mathbf{q},\mathbf{q};\mathbf{k}-\mathbf{q}',\mathbf{q}'}(t_1)\approx G^{11^{-1}}_{\mathbf{k}-\mathbf{q}}(t_1)\circ G^{11^{-1}}_{\mathbf{q}}(t_1)\,\delta_{\mathbf{q}\mathbf{q}'}\\ +G^{11^{-1}}_{\mathbf{k}-\mathbf{q}}(t_1)\bullet G^{11^{-1}}_{\mathbf{q}}(t_1)\,\delta_{\mathbf{k}\mathbf{q}-\mathbf{q}'}.\end{aligned}$$

Inserting these expressions into Eq. (A1) and using Eq. (17) yields

$$\begin{aligned}\bar{M}^{112}_{\mathbf{k}-\mathbf{q};\mathbf{q};\mathbf{k}-\mathbf{q}',\mathbf{q}'}\approx G^{11^{-1}}_{\mathbf{k}-\mathbf{q}}(t_2)\cdot G^{11}_{\mathbf{k}-\mathbf{q}}(t_2+t_1)\cdot G^{11^{-1}}_{\mathbf{k}-\mathbf{q}}(t_1)\circ\mathbf{1}\delta_{\mathbf{q}\mathbf{q}'}\\ +G^{11^{-1}}_{\mathbf{k}-\mathbf{q}}(t_2)\cdot G^{11}_{\mathbf{k}-\mathbf{q}}(t_2+t_1)\cdot G^{11^{-1}}_{\mathbf{k}-\mathbf{q}}(t_1)\bullet\mathbf{1}\delta_{\mathbf{q}\mathbf{q}'}\\ \approx\mathbf{1}\circ\mathbf{1}\delta_{\mathbf{q}\mathbf{q}'}+\mathbf{1}\bullet\mathbf{1}\delta_{\mathbf{k}-\mathbf{q},\mathbf{q}'}\,,\end{aligned} \tag{A2}$$

where $\mathbf{1}^{ac}=\delta_{ac}$.

Finally, Eq. (A2) and the relation $\bar{M}_{211}=K_{22}*(\bar{M}_{11*2})^{*}*K_{11}^{-1}$ give the leading N-order expression for M_{211},

$$\bar{M}^{211}_{\mathbf{k}-\mathbf{q}'+\mathbf{q},\mathbf{q}';-\mathbf{q};\mathbf{k}}\approx K_{\mathbf{q}}\circ\mathbf{1}\delta_{\mathbf{k}\mathbf{q}'}+\mathbf{1}\bullet K_{\mathbf{q}}\delta_{\mathbf{q}\mathbf{q}'} \tag{A3}$$

to lowest order in the mode-coupling parameter M/N. It interesting that the first term in Eq. (43) gives the only contribution to M_{211} at order $(M/N)^0$: In other words, when mode-coupling corrections are neglected, the term involving the fluctuating forces in Eq. (43) can be dropped.

Note that in this appendix, we have allowed ourselves to neglect the difference between the inverse of quantities on the multilinear level and the linear-linear sub-block level, which is correct to order $(M/N)^0$ and consistent with the level of approximation of the rest of the derivation of Eqs. (A2) and (A3).

APPENDIX B: SYMMETRY PROPERTIES OF $G_{\alpha\beta}(t)$ AND $\bar{M}_{\alpha\beta}$

In the ideal gas case, the Q_α's are either even or odd functions of momentum. This property implies that the elements of the multilinear basis set Q_α are either symmetric or antisymmetric under the time-reversal operator $\mathcal{T}$, which reverses the momenta. Mathematically, this property can be written as $\mathcal{T}Q_\alpha=\gamma_\alpha Q_\alpha$, where γ_α is either 1 if α contains an even number of momenta indices, or -1 when it has an odd number. In addition, there typically is a symmetry under the reflection operator $\mathcal{R}$, which inverts both the momenta and the positions of all particles. As the basis set elements Q_α depends on the spatial degrees of freedom through $\exp(i\mathbf{k}\cdot\mathbf{r}_j)$ [see Eq. (55)], it follows that $\mathcal{R}Q_\alpha=\gamma_\alpha Q^*_\alpha$. These relations also holds for other systems in which the potential energy depends only on the distances between particles in the system. These two symmetries plus time translation invariance have the following implications for $\bar{M}_{\alpha\beta}$ and $G_{\alpha\beta}(t)$ (see also Ref. [57]).

As the equilibrium distribution function is invariant under $\mathcal{R}$,

$$C_{\alpha\beta}(t)=\langle Q_\alpha(t)Q^*_\beta\rangle=\langle[\mathcal{R}Q_\alpha(t)](\mathcal{R}Q^*_\beta)\rangle=\gamma_\alpha\gamma_\beta C^*_{\alpha\beta}(t). \tag{B1}$$

Hence, if $\gamma_\alpha\gamma_\beta=1$, the imaginary part is zero, otherwise the real part is zero. Since the wave-vector dependence of the densities always enters in the form of i times a wave vector, imaginary correlation functions must be odd functions of the wave vector and real correlation functions must be even functions of wave vector, provided these quantities are analytic in wave vector.

Time reversal invariance $\mathcal{T}e^{\mathcal{L}t}=e^{-\mathcal{L}t}\mathcal{T}$ yields

$$\begin{aligned}\langle(e^{\mathcal{L}t}Q_\alpha)Q^*_\beta\rangle&=\langle(\mathcal{T}e^{-\mathcal{L}t}\mathcal{T}Q_\alpha)Q^*_\beta\rangle=\langle(e^{-\mathcal{L}t}\mathcal{T}Q_\alpha)\mathcal{T}Q^*_\beta\rangle\\&=\gamma_\alpha\gamma_\beta\langle(e^{-\mathcal{L}t}Q_\alpha)Q^*_\beta\rangle,\end{aligned}$$

which, combined with Eq. (B1), implies that $K_{\alpha\beta}$ is real and symmetric, and hence $G_{\alpha\beta}(t)=\gamma_\alpha\gamma_\beta G_{\alpha\beta}(-t)$. This can be combined with Eq. (B1) to yield

$$G_{\alpha\beta}(t)=G^*_{\alpha\beta}(-t). \tag{B2}$$

So from Eqs. (B1) and (B2), we conclude that if $\gamma_\alpha\gamma_\beta=1$, $G_{\alpha\beta}(t)$ is real, even in wave vectors, and symmetric under $t\to-t$, whereas if $\gamma_\alpha\gamma_\beta=-1$, it is imaginary, odd in wave vectors, and antisymmetric under time reversal. As $\bar{M}=[dG(t)/dt]G^{-1}(t)$, this also implies that $\bar{M}_{\alpha\beta}$ is real and even in wave vectors if $\gamma_\alpha\gamma_\beta=1$, and imaginary and odd in wave vector otherwise.

The following ordering is now valid when the magnitudes of the wave vectors are small. Imaginary correlation functions and vertices, being odd in the wave-vector arguments, are typically of linear order in the wave vectors. But as the vertices $\bar{M}$ contain time derivatives, they will always be at least of the order of the wave vectors, so a real-valued vertex is at least quadratic in wave vector, whereas a real-valued correlation function is typically of order one.

Finally, using time-translation invariance, $G_{\alpha\beta}(t)=G^*_{\hat\beta\hat\alpha}(-t)K_{\hat\alpha\alpha}K^{-1}_{\beta\hat\beta}$, which conveniently combines with Eqs. (B2) to give

$$G_{\alpha\beta}(t)=G_{\hat\beta\hat\alpha}(t)K_{\hat\alpha\alpha}K^{-1}_{\beta\hat\beta}. \tag{B3}$$

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