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Overdamped van Hove function of colloidal suspensions

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The generalized-hydrodynamic theory for collective diffusion of a monodisperse colloidal suspension is developed in the framework of the Onsager-Machlup theory of time-dependent fluctuations. The time evolution of the intermediate scattering function $F(k,t)$ is derived as a contraction of the description involving the instantaneous particle number concentration, the particle current, and the stress tensor of the Brownian fluid as state variables. We show that the proper overdamped limit of this equation requires the explicit separation of the stress tensor in its mutually orthogonal kinetic and configurational contributions. Analogous results also follow for the self-intermediate scattering function $F_s(k,t)$. We show that neglecting the non-Markovian part of the configurational stress tensor memory, one recovers the single exponential memory approximation (based on sum rules derived from the Smoluchowski equation) for both $F_s(k,t)$ and $F(k,t)$. We suggest simple approximate manners to relate the collective and the self-memory functions, leading to Vineyard-like approximate relations between $F_s(k,t)$ and $F(k,t)$.

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I. INTRODUCTION

The most fundamental dynamic property of a colloidal suspension in thermodynamic equilibrium is the so-called van Hove function $G(r,t)$. This is [1,2] the time-dependent correlation function of the fluctuation $\delta n(\mathbf{r},t)$ of the instantaneous local concentration of colloidal particles, $n(\mathbf{r},t)$, at position $\mathbf{r}$ and time t, around its bulk equilibrium value n, i.e., $G(|\mathbf{r}-\mathbf{r}'|,t)\equiv\langle\delta n(\mathbf{r},t)\delta n(\mathbf{r}',0)\rangle$, with $\delta n(\mathbf{r},t)\equiv n(\mathbf{r},t)-n$. Dynamic light scattering techniques [3,4] allow the experimental determination of this function, or, rather, of its spatial Fourier transform $F(k,t)$, referred to as the intermediate scattering function. $G(r,t)$, or $F(k,t)$, contains all the relevant information on the macroscopic dynamic behavior of the suspension. Thus the basic goal of a statistical mechanical theory of colloid dynamics consists of the derivation of a macroscopic equation for $G(r,t)$ or $F(k,t)$ starting from a microscopic level of description. Although a colloidal suspension is formed by N colloidal particles plus all the atoms or molecules that constitute the solvent, averaging out the microscopic degrees of freedom of the solvent molecules (and other molecular species, such as salt ions) leads to a solvent-averaged dynamic description involving only the degree of freedom of the N colloidal particles, i.e., the many-body Langevin equation [5]. It is generally accepted that this system of N stochastic equations for the velocities of the N colloidal particles, coupled together by the direct and hydrodynamic interaction forces between the particles, constitute an adequate microscopic description of the dynamics of the suspension. Thus the crux of the statistical mechanical theory of colloid dynamics consists of the derivation of a time-evolution equation for the macroscopic variable $\delta n(\mathbf{r},t)$, starting from the microscopic description provided by the N-particle Langevin equation. There is, however, not a unique or canonical route to carry out such derivation [6,7], and the development of the statistical mechanical theory of colloid dynamics within the last 20 years consists of a rather rich variety of attempts to carry out this derivation along a few alternative routes. Although many important issues have been addressed and understood [4,8,7,9], a few essential points still merit further and careful discussion. For example, any theory for $F(k,t)$ properly rooted in N-particle Langevin equation dynamics should lead to expressions for $F(k,t)$ valid for all time regimes associated to the Brownian motion of the colloidal particles [10,11] . The regime relevant to the dynamic light scattering experiments [3], however, corresponds to times much longer than the typical relaxation time $\tau_B=\zeta^0/M$, where M is the mass of each particle, and ζ^0 is its friction coefficient in the absence of interactions. In the so-called diffusive regime $t\gg\tau_B$, the initial velocities of the Brownian particles have been completely damped out by the friction of the solvent, and $\delta n(\mathbf{r},t)$ relaxes only through purely diffusive mechanisms. Thus one has to take the so-called overdamped limit $t\gg\tau_B$ in any general time-evolution equation for $\delta n(\mathbf{r},t)$ [or on the corresponding expression for $G(r,t)$], obtained from a derivation rooted in the microscopic dynamics represented by the N-particle Langevin equations. This full program was carried out by Hess and Klein [12] in their pioneering work on colloid dynamics, although they based their derivations on the N-particle Fokker-Planck equation, rather than on the N-particle Langevin equation. In the absence of hydrodynamic interactions, however, there is full equivalence between these two microscopic descriptions [13]. In fact, Hess and Klein explained and discussed the procedure for taking the overdamped limit in the general expressions obtained for $F(k,t)$. From their discussion [12], however, it becomes clear that this issue is at least subtle and delicate. Although the physical concepts are clear, the actual formal procedure for taking this limit still deserves additional attention. Addressing this delicate point is just one of the main objectives of the present work.

Here we derive a general expression for $F(k,t)$ rooted in

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the microscopic dynamics contained in the N-particle Langevin equation. At the present point, to simplify matters, we keep in mind a monodisperse suspension in the absence of hydrodynamic interactions, and will only consider direct interactions describable by continuous effective pair potentials. For this system, we derive a general expression for $F(k,t)$ in terms of static structural properties of the suspension [assumed determined by statistical thermodynamic methods [1], given the pair potential $u(r)$], and of a memory function associated with the time-dependent correlation function of the stress tensor of the colloidal fluid. Up to this point, our derivation parallels that of Hess and Klein, since, in the absence of hydrodynamic interactions, the statistical mechanical equivalence between the respective microscopic starting points (i.e., the N-particle Langevin equation and the Fokker-Planck equation) is free from ambiguities [13]. In the next step, however, we provide our own approach to the problem of taking the overdamped limit of the general expression for $F(k,t)$. For this, we found that the use of the generalized Langevin equation (GLE) formalism, along with the concept of contraction of the description [14], is particularly useful. As a consequence, we obtain the main result of this paper, namely, a general expression for $F(k,t)$ in the overdamped limit, written in terms of purely static structural properties and of the memory funcion associated with the time-correlation function of the *configurational* component of the stress tensor. The main value of our present derivation is its conceptual simplicity (although some details may require careful, and sometimes extensive, statistical mechanical derivations, which are, however, straightforward). In particular, the physical assumptions behind the proper manner of taking the overdamped limit are formally stated in clear and rigourous terms.

The first part of this paper will have a rather pedagogical style. Thus, in Sec. II we briefly review a few important aspects of the theory of colloid dynamics, and the various possible strategies to derive general expressions for $F(k,t)$. In Sec. III we explain and illustrate the use of the GLE formalism to describe collective diffusion in colloidal systems. The GLE formalism is most commonly understood as the result of a formal derivation of a time-evolution equation for a macroscopic variable, starting from the microscopic N-particle dynamics, by a systematic application of projection operators [15]. This leaves the impression that the full structure of the resulting time-evolution equation is a direct consequence of the underlying microscopic dynamics. In reality, the most relevant features of the macroscopic time-evolution equation of the macroscopic variable are a direct consequence of mathematical symmetry conditions, such as the stationarity condition, or the time-reversal symmetry of the macroscopic variables [14]. Thus, for the GLE formalism, we prefer to understand the systematic application of the Onsager-Machlup [16] general theory of time-dependent fluctuations, along with the process of contraction of the description [14]. This theoretical framework allows us to write quite a few of the most important features of the macroscopic time-evolution equation without resorting to the underlying microscopic description. Only at a latter stage, the microscopic dynamics can be employed to determine additional elements of the time-evolution equation that were left undetermined by the ‘‘selection rules’’ that derive from general symmetry considerations. The end result of our application to colloid dynamics is an expression for $F(k,t)$ in terms of a hierarchy of memory functions. At this point, the reader will recognize that our derivations are just a straightforward translation to colloids of the corresponding derivations for molecular liquids, as reviewed in Boon and Yip’s textbook [2]. In fact, some of the results for $F(k,t)$ for a simple liquid correspond to the frictionless limit of our results in Sec. III. The main addition in our work is the treatment of the oposite limit, i.e., the derivation of the general expression for $F(k,t)$ of a colloidal system in the overdamped limit. This is described in detail in Sec. IV, which constitutes the main contribution of this paper. In reality, these results, besides their intrinsic interest, constitute a basic ingredient of a program aimed at constructing a fully self-consistent theory of colloid dynamics. Some aspects of this program, and of its concrete applications, are briefly described in Sec. V.

II. GENERAL CONCEPTS

Let us consider a monodisperse colloidal suspension in the absence of hydrodynamic interactions. For our present purpose, we assume that the microscopic dynamics of this system, formed by N spherical particles in a volume V, can be described by the N-particle Langevin equations [3–5]

$$M\frac{d\mathbf{v}_i(t)}{dt}=-\zeta^o\mathbf{v}_i(t)+\mathbf{f}_i(t)+\sum_{j\neq i}\mathbf{F}_{ij}(t)\qquad(i=1,2,\ldots,N). \tag{2.1}$$

In these equations, M is the mass, and $\mathbf{v}_i(t)$ the velocity of the ith particle, and ζ^o is its friction coefficient in the absence of interactions. Also, $\mathbf{f}_i(t)$ is a random force, modeled as a Gaussian white noise of zero mean, and variance given by $\langle\mathbf{f}_i(t)\mathbf{f}_j(0)\rangle=k_BT\zeta^o2\,\delta(t)\delta_{ij}\overleftrightarrow{\mathbf{I}}$ ($i,j=1,2,\ldots,N$; $\overleftrightarrow{\mathbf{I}}$ is the 3×3 unit tensor). The direct interactions between the particles are represented by the sum of the pairwise forces $\mathbf{F}_{ij}$ that the jth particle exerts on particle i, i.e., $\mathbf{F}_{ij}$ is obtained from the pair potential $u(|\mathbf{r}_i-\mathbf{r}_j|)$. The statistical mechanical information contained in this description can also be cast in terms of the corresponding N-particle Fokker-Planck equation [17] for the probability $W(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{v}_1,\mathbf{v}_2,..;t)$ that particle i has position $\mathbf{r}_i$ and velocity $\mathbf{v}_i$ at time t,

$$\frac{\partial W(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{v}_1,\mathbf{v}_2,..;t)}{\partial t}=O_{FP}W(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{v}_1,\mathbf{v}_2,..;t), \tag{2.2}$$

where O_{FP} is the Fokker-Planck operator [12].

Equations (2.1) and (2.2) are equivalent representations of the same dynamical description. Acording to Eq. (2.1), the initial decay of the particles’ velocities is determined by the frictional damping of the solvent, and this defines a time scale $\tau_B\equiv M/\zeta^o$. For times $t\gg\tau_B$, normally probed in dynamic light scattering experiments, the dynamics is purely diffusive. Thus, one can ‘‘tune’’ this microscopic description to the diffusive regime by taking the limit $t\gg\tau_B$ in Eqs. (2.1). This amounts to neglecting the inertial terms in these equations, thus leading to the *overdamped* N-particle Langevin equation [18]

$$\frac{d\mathbf{r}_i(t)}{dt} \equiv \frac{\mathbf{f}_i(t)}{\zeta^o} + \sum_{j \neq i} \frac{\mathbf{F}_{ij}(t)}{\zeta^o} \quad (i=1,2,\ldots,N). \tag{2.3}$$

Just as for the original Langevin equations, one can express the same information in Eq. (2.3), in the Fokker-Planck language, i.e., in terms of an equation for the probability distribution $W(\mathbf{r}_1, \mathbf{r}_2 \ldots ; t)$ that a particle i has a position $\mathbf{r}_i$ at a time t. Such an equation is called the Smoluchowski equation, and can be written as

$$\frac{\partial W(\mathbf{r}_1, \mathbf{r}_2 \ldots ; t)}{\partial t} = O_S W(\mathbf{r}_1, \mathbf{r}_2 \ldots ; t), \tag{2.4}$$

where O_S is the Smoluchowski operator [6]. The same equation can also be derived from the Fokker-Planck equation [17].

The following conceptually important task is to derive, from any of the four descriptions above, the properties of the intermediate scattering function. In doing so, we can distinguish various approaches and strategies. These may differ depending on their goals and on the general approach they use to derive the macroscopic information contained in $F(k,t)$ from the microscopic description in the equations above. What follows is a schematic summary of the main approaches and results in this direction.

(1) Start from the already overdamped microscopic description provided by either Eqs. (2.3) or (2.4). Ackerson [6] chose to start from the Smoluchowski equation, and applied the projection operator formalism to derive the relaxation equation for $F(k,t)$, which he found to have the general structure

$$\frac{\partial F(k,t)}{\partial t} = -k^2 D_0 S^{-1}(k) F(k,t) + \int_0^t M(k,t-t') S^{-1}(k) F(k,t') dt', \tag{2.5}$$

where $S(k) \equiv F(k,t=0)$ is the static structure factor, $D_0 \equiv k_B T/\zeta^0$ is the short-time self-diffusion coefficient, and $M(k,t)$ is a memory function which contains the effects of the direct interactions. For this function, Ackerson wrote an expression involving projection operators related to the Smoluchowski operator [6]. This expression is mostly a formal result, not very useful for practical calculations, except in certain limiting conditions. However, it is a convenient starting point for the calculation of the first few moments of $F(k,t)$. These are the coefficients of the short-time expansion of $F(k,t)$, defined as

$$F(k,t) = \sum_{n=0}^{\infty} \frac{m^{(n)}(k)}{n!} t^n. \tag{2.6}$$

Thus the moment $m^{(n)}(k)$ is the initial value of the nth time derivative of $F(k,t)$. Clearly, $m^{(0)}(k) = S(k)$, and, from Eq. (2.5), it is easy to see that $m^{(1)}(k) = -k^2 D_0 S^{-1}(k)$. These are two exact moment conditions, assuming the microscopic dynamics to be described by the Smoluchowski equation. Ackerson also calculated the second moment $m^{(2)}(k)$, for which he found

$$m^{(2)}(k) = k^4 D_0^2 + n D_0 \int d\mathbf{r}\, g(r) [1 - \cos(\mathbf{k} \cdot \mathbf{r})] \times (\mathbf{k} \cdot \boldsymbol{\nabla})^2 \beta u(r), \tag{2.7}$$

where $g(r)$ is the radial distribution function of the colloidal particles, and $u(r)$ is the pair potential. Arauz-Lara and Medina-Noyola [19] extended these calculations to the third moment $m^{(3)}(k)$, with the result

$$\begin{aligned} m^{(3)}(k) = {} & -k^6 D_0^3 - 3 D_0^3 k^2 n \int d\mathbf{r}\, g(r) (\mathbf{k} \cdot \boldsymbol{\nabla})^2 \beta u(r) \\ & - 2 D_0^3 n \int d\mathbf{r}\, g(r) \sin(\mathbf{k} \cdot \mathbf{r}) (\mathbf{k} \cdot \boldsymbol{\nabla})^3 \beta u(r) \\ & - 2 D_0^3 n \int d\mathbf{r}\, g(r) [1 - \cos(\mathbf{k} \cdot \mathbf{r})] [(\mathbf{k} \cdot \boldsymbol{\nabla}) \nabla \beta u(r)]^2 \\ & - D_0^3 n^2 \int d\mathbf{r}' d\mathbf{r}\, g(\mathbf{r}, \mathbf{r}') \{1 - 2 \cos(\mathbf{k} \cdot \mathbf{r}) \\ & + \cos[(\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}'))]\} (\mathbf{k} \cdot \boldsymbol{\nabla}) (\mathbf{k} \cdot \boldsymbol{\nabla}') \\ & \times (\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}) \beta u(r) \beta u(r') \end{aligned} \tag{2.8}$$

where $g^{(3)}(\mathbf{r}, \mathbf{r}')$ is the three-particle correlation function. These same results for $m^{(2)}(k)$ and $m^{(3)}(k)$ were also derived by Pusey and Tough [18] starting from the other representation of the overdamped microscopic dynamics, namely, the overdamped many-particle Langevin equation in Eq. (2.3). Similar results were also derived in parallel for $F_s(k,t)$. Besides these results for the short-time properties of the intermediate scattering functions, the methods above do not lead to a practical prescription for the full calculation of these dynamic properties. However, a simple approximation for the full time dependence of $F(k,t)$ and $F_s(k,t)$, based on these exact moment conditions, was suggested by Arauz-Lara and Medina-Noyola [19]. This consists of assuming a simple functional form for the memory function $M(k,t)$ [and for its self-counterpart $M_s(k,t)$], namely, a single exponential, with its k-dependent amplitude and decay constants fixed by the short-time conditions above. This approximation is about the simplest, yet reasonably accurate, approach to the quantitative calculation of the dynamic properties of a colloidal suspension. Although most of its concrete applications have been related to self-diffusion phenomena [7], recently its usefulness and limitations were demonstrated in the analysis of simulated and experimental results for *collective* diffusion in quasi-two-dimensional suspensions [20,21].

Let us mention that other approaches also derive information on $F(k,t)$ and/or $F_S(k,t)$ starting from the N-particle Smoluchowski equation. These include the application of linear response theory [22,23] or kinetic-theoretical methods [24,25]. We do not refer in detail to these contributions either because they do not relate directly to the present work, or because they refer to more specific conditions or to effects (such as hydrodynamic interactions) that we explicitly wish to leave aside for the moment. These contributions, however, were described in recent reviews of the field [4,7].

(2) Start from the microscopic description without overdamping, provided either by the many-body Langevin equation [Eq. (2.1)] or its equivalent Fokker-Planck equation [Eq.

(2.2)]; derive results for $F(k,t)$, and then take the overdamped limit. To some extent, this is a more general approach, since the results for $F(k,t)$ before overdamping describe, in principle, the dynamics of the colloidal suspension not only in the diffusive regime, but also at earlier times, comparable to τ_B. However, to compare with light scattering measurements, the overdamped limit has to be taken. The approach followed by Hess and Klein [12] belongs to this second strategy, as does our present derivations of the collective diffusion properties explained in the following sections. Hess and Klein based their derivations on the Fokker-Planck equation, whereas we take the elements of the microscopic dynamics needed in our work from the many-body Langevin equation. Thus from the formal equivalence between these two microscopic descriptions, one should expect the same ultimate results for both theories. There is, however, an additional conceptual parallelism between Hess and Klein's work and the present work. This refers to the use of the general theory that we refer to as the generalized Langevin equation. The application of this formalism in the context of simple liquids is referred to as generalized hydrodynamics [2], which Hess and Klein adapted to colloidal suspensions. In their work [12], however, the generality of their treatment, and their thorough analysis using linear response theory and projection operator techniques, hide somewhat the intrinsic simplicity of the GLE formalism, which we strongly emphasize in this work.

In this second general strategy, once the general results for $F(k,t)$ have been derived, the overdamped limit has to be taken. This is a particularly subtle issue, and merits a careful and explicit discussion. The physical arguments and the end results in Hess and Klein's work are accurate, but are not explicitly detailed. In contrast, this will be the main subject of the present work. Closely related to this issue is the equivalence between the results obtained from this second strategy, after the overdamped limit has been taken, and the results of the alternative strategy in (1). This issue gave rise to considerable initial confusion [12,26], which was clarified only in 1986 by Cichocki and Hess [26,27]. These authors used projection operators techniques to establish the formal relationship between the memory functions that naturally emerge from the application of these two alternative stragegies. In our present work we will also discuss some aspects related to this issue. In particular, the moment conditions obtained after overdamping will be compared with the corresponding conditions obtained from the overdamped microscopic descriptions. This will be discussed below within our own theoretical approach.

III. GLE FOR COLLECTIVE DIFFUSION

The two strategies above emphasize the notion that the structure of the dynamic equation for $F(k,t)$ or $F_S(k,t)$ must be rooted entirely on the underlying microscopic dynamics provided by either of the descriptions represented by Eqs. (2.1)–(2.4) above. In reality, however, some of the most important features of the time evolution equations for $F(k,t)$ and $F_S(k,t)$ can be written right at the outset, since they derive from rather general selection rules [14] originating from the stationarity condition, and from other symmetry properties of the macroscopic variables whose dynamics couple to the dynamics of the local particle concentration.

In the present paper we adopt this approach, following the work of Alarcon-Waess and Medina-Noyola [28]. Thus we write the most general time-evolution equation for the fluctuations of the local concentration $n(\mathbf{r},t)$ of colloidal particles, which is consistent with the selection rules referred to above. Specific information about the microscopic dynamics is then employed in the approximate or partial determination of those elements of the time-evolution equation that such selection rules leave undetermined.

The basis of this appoach, then, is the general mathematical conditions that the local concentration $n(\mathbf{r},t)$, or any other variable or set the variables that describe fluctuations around the equilibrium state, must satisfy. These general conditions are stated by the theorem of stationarity [14]. According to this theorem, the most general linear stochastic differential equation that describes a (multivariable) stationary stochastic process $\mathbf{a}(t)=[a_1(t),a_2(t),\ldots,a_\nu(t)]$, must have the structure [14],

$$\frac{d\mathbf{a}(t)}{dt}=-\omega\chi^{-1}\mathbf{a}(t)-\int_0^t L(t-t')\chi^{-1}\mathbf{a}(t')dt'+\mathbf{f}(t), \tag{3.1}$$

where χ is the matrix of static correlations, $\chi_{ij}\equiv\langle a_i(0)a_j^*(0)\rangle$, ω is an anti-Hermitian matrix ($\omega_{ij}=-\omega_{ji}^*$), and the matrix $L(t)$ is determined by the fluctuation-dissipation relation $L_{ij}(t)=\langle f_i(t)f_j(0)\rangle$, where $f_i(t)$ is the ith component of the vector of random forces $\mathbf{f}(t)$.

In the present application of this theorem, we shall consider $a_1(t)$ to be the Fourier transform $\delta n(\mathbf{k},t)$ of the fluctuations $\delta n(\mathbf{r},t)\equiv n(\mathbf{r},t)-n$ of the local concentration $n(\mathbf{r},t)$ around its bulk value n. $n(\mathbf{k},t)$ will be normalized such that its time-independent correlation is $\chi_{nn}(k)\equiv\langle\delta n(\mathbf{k},0)\delta n(-\mathbf{k},0)\rangle=S(k)$, where $S(k)$ is the static structure factor of the bulk suspension.

If we choose the least detailed description ($\nu=1$), i.e., $\mathbf{a}(t)\equiv[a_1(t)]=[\delta n(\mathbf{k},t)]$, then Eq. (3.1) reads

$$\frac{\partial\delta n(\mathbf{k},t)}{\partial t}=-\int_0^t L(k,t-t')S^{-1}(k)\delta n(\mathbf{k},t')dt'+f(\mathbf{k},t), \tag{3.2}$$

since the only element of ω vanishes. In this equation, $f(\mathbf{k},t)$ represents the random diffusive fluxes, whose time-dependent correlation function is given by the fluctuation dissipation relation $\langle f(\mathbf{k},t)f(-\mathbf{k},0)\rangle=L(k,t)$. Multiplying Eq. (3.2) by $\delta n(-\mathbf{k},0)$, and taking the equilibrium ensemble average, we are led to the time-evolution equation for $F(k,t)$, whose solution, in Laplace space, reads

$$F(k,z)=\frac{S(k)}{z+L(k,z)S^{-1}(k)}. \tag{3.3}$$

At this minimal level of description (i.e., $\nu=1$), the GLE approach is unable to go further in revealing the structure of the memory function $L(k,t)$. Thus, although this is the most general and exact time-evolution equation for $F(k,t)$, it is also the least useful. For example, from Eq. (3.3) we can exactly calculate only the obvious zeroth moment condition

$m^{(0)}(k)=S(k)$, since the higher order moments $m^{(n)}(k)$ ($n \geqslant 1$) depend on $L(k,z)$, which is unknown. The idea, however, is to consider next a more detailed description, i.e., Eq. (3.1) with $\nu > 1$, and then contracting down to this minimal description. As an illustration, let us write the continuity equation for $n(\mathbf{k},t)$. For this, we do need the information contained in the microscopic definition of $\delta n(\mathbf{k},t)$,

$$\delta n(\mathbf{k},t)=\frac{1}{\sqrt{N}}\sum_{i=1}^{N} e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}, \tag{3.4}$$

where $\mathbf{r}_i(t)$ is the position of the ith colloidal particle at time t. Taking the time derivative of $\delta n(\mathbf{k},t)$ we have an exact equation, namely, the continuity equation

$$\frac{\partial \delta n(\mathbf{k},t)}{\partial t}=ik\,\delta j_l(\mathbf{k},t), \tag{3.5}$$

where $\delta j_l(\mathbf{k},t)\equiv j_l(\mathbf{k},t)=\hat{\mathbf{k}}\cdot\mathbf{j}(\mathbf{k},t)$ is the component of the current $\mathbf{j}(\mathbf{k},t)$ in the direction $\hat{\mathbf{k}}$ of the vector $\mathbf{k}$, i.e.,

$$j_l(\mathbf{k},t)=\frac{1}{\sqrt{N}}\sum_{i=1}^{N} \hat{\mathbf{k}}\cdot\mathbf{v}_i(t)e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}, \tag{3.6}$$

with $\mathbf{v}_i(t)=d\mathbf{r}_i(t)/dt$. Thus let us now define $\mathbf{a}(t) \equiv [\delta n(\mathbf{k},t), \delta j_l(\mathbf{k},t)]$, whose static correlation matrix χ is

$$\chi=\begin{bmatrix} S(k) & 0 \\ 0 & \chi_{jj} \end{bmatrix}, \tag{3.7}$$

with $\chi_{jj}=k_BT/M$. From the exact continuity equation, and keeping in mind the general structure for the time-evolution equation of $\mathbf{a}(t)$ in Eq. (3.1), we read that $\omega_{nj}\chi_{jj}^{-1}=-ik$, and that $L_{nn}(\mathbf{k},t)=L_{nj}(\mathbf{k},t)=0$. Hence Eq. (3.1), with $\nu=2$, reads

$$\frac{\partial \delta n(\mathbf{k},t)}{\partial t}=-\omega_{nj}\chi_{jj}^{-1}\delta j_l(\mathbf{k},t), \tag{3.8}$$

$$\frac{\partial \delta j_l(\mathbf{k},t)}{\partial t}=-\omega_{jn}S^{-1}(k)\delta n(\mathbf{k},t) - \int_0^t L_{jj}(k,t-t')\chi_{jj}^{-1}\delta j_l(\mathbf{k},t')dt' + f_l(\mathbf{k},t), \tag{3.9}$$

where $\omega_{nj}=-\omega_{jn}^{*}=-ik\chi_{jj}$.

The next step is to contract this description, i.e., to eliminate $\delta j_l(\mathbf{k},t)$ from this set of equations. This leads to an equation that has a richer structure than Eq. (3.2) [or, for that matter, than Eq. (3.3) for $F(k,z)$]. In terms of $F(k,z)$, the resulting equation can be written as Eq. (3.3) itself, but with $L(k,z)$ now having the following general structure:

$$L(k,z)=\frac{k^2\chi_{jj}}{z+L_{jj}(k,z)\chi_{jj}^{-1}}. \tag{3.10}$$

Thus this exercise revealed additional features of the time-evolution equation of $\delta n(\mathbf{k},t)$, more specifically of the actual structure of the memory function $L(k,t)$. As a result, from Eq. (3.3) with Eq. (3.10), we can calculate exactly, in addition to $m^{(0)}(k)$, the first and second moment conditions $m^{(1)}(k)=0$ and $m^{(2)}(k)=-k^2/M\beta$. Still, the only new information is basically that derived from the continuity equation, namely, the k^2 dependence of $L(k,t)$. Thus there is nothing in these results that refers specifically to our actual system of Brownian particles. Furthermore, the time scale $\tau_B\equiv M/\zeta^0$ does not yet appear explicitly, and, hence, we cannot take the overdamped limit $z \ll z_B \equiv \tau_B^{-1}$ in Eqs. (3.3) and (3.10). Such specific information must be drawn from the assumed underlying microscopic dynamics. In our example, this is done as follows. If we take the time derivative of the current in Eq. (3.6), and employ the N-particle Langevin equation [Eq. (2.1)], we are led to the result

$$\frac{\partial \delta j_l(\mathbf{k},t)}{\partial t}=-\frac{\zeta^0}{M}\delta j_l(\mathbf{k},t)+\frac{f^0(\mathbf{k},t)}{M} + \frac{1}{\sqrt{N}}\sum_{i=1}^{N}\hat{\mathbf{k}}\cdot\frac{\mathbf{F}_i(t)}{M}e^{i\mathbf{k}\cdot\mathbf{r}_i(t)} + \frac{ik}{\sqrt{N}}\sum_{i=1}^{N}[\hat{\mathbf{k}}\cdot\mathbf{v}_i(t)]^2 e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}, \tag{3.11}$$

where

$$f^0(\mathbf{k},t)\equiv\frac{1}{\sqrt{N}}\sum_{i=1}^{N}\hat{\mathbf{k}}\cdot\mathbf{f}_i(t)e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}, \tag{3.12}$$

and $\mathbf{F}_i(t)\equiv\Sigma_{j\neq i}\mathbf{F}_{ij}(t)$. Clearly, the first two terms on the right-hand side of this equation derive from the first two terms of the right-hand side of Eq. (2.1). They describe the effect of the friction of the solvent on each colloidal particle. Although it is not possible to establish the detailed correspondence of the other terms with each of the terms on the right-hand side of Eq. (3.9), the previous result indicates that the memory function $L_{jj}(k,t)$ should be written, to exhibit explicitly the first term in Eq. (3.11) above, as

$$L_{jj}(k,z)=\frac{\zeta^0}{M}\chi_{jj}+\Delta L_{jj}(k,z). \tag{3.13}$$

This leads to the following expression for $F(k,z)$:

$$F(k,z)=\cfrac{S(k)}{z+\cfrac{k^2S^{-1}(k)\chi_{jj}}{z+\cfrac{\zeta^0}{M}+\Delta L_{jj}(k,z)\chi_{jj}^{-1}}}. \tag{3.14}$$

Clearly, this is a still more useful result than that in Eq. (3.3) with Eq. (3.10). In fact, several interesting limiting conditions can be obtained from Eq. (3.14). The first of them refers to the short-time moment conditions. In addition to

$$m^{(0)}(k)=S(k), \tag{3.15}$$

$$m^{(1)}(k)=0, \tag{3.16}$$

and

$$m^{(2)}(k)=-\frac{k^2}{M\beta} \tag{3.17}$$

[already determined by Eq. (3.3) with Eq. (3.10)], Eq. (3.14) also exactly determines the third moment

$$m^{(3)}(k)=\frac{k^2\chi_{jj}\zeta^0}{M}, \tag{3.18}$$

which now involves the Brownian frecuency $z_B=\zeta^0/M$.

The other limiting condition that can be considered from Eq. (3.14) refers to the structure of $F(k,z)$ in the overdamped limit $z/z_B \ll 1$. Assuming that the only relevant dependence of $F(k,z)$ on z_B is that explicitly exhibited in Eq. (3.14), and assuming that $\lim_{z/z_B\to 0}\Delta L_{jj}(k,z)/z_B \neq 0$, we find that the overdamped limit of Eq. (3.14) is

$$F(k,z)=\frac{S(k)}{z+\dfrac{k^2D_0S^{-1}(k)}{1+D_0M^2\beta^2\Delta L_{jj}(k,z)}}, \tag{3.19}$$

with $D_0\equiv k_BT/\zeta^0$. Clearly, this equation, describing the diffusive dynamics of the suspension, should lead to different short-time conditions than those in Eqs. (3.15)–(3.18). In fact, the exact moment conditions that can be derived from Eq. (3.19) are

$$m^{(0)}(k)=S(k), \tag{3.20}$$

$$m^{(1)}(k)=-k^2D_0, \tag{3.21}$$

which coincide with the ''Smoluchowskian'' moment conditions derived by Ackerson. The higher-order moments $m^{(n)}(k)$, $n\geqslant 2$, now depend on $\Delta L_{jj}(k,z)$, which is as yet undetermined. Equation (3.19) is in reality equivalent to Ackerson's memory equation [Eq. (2.5)], and this equivalence can be expressed by writing Ackerson's memory function $M(k,t)$ in terms of our memory function $\Delta L_{jj}(k,t)$ as follows:

$$M(k,z)=k^2D_0\frac{D_0M^2\beta^2\Delta L_{jj}(k,z)}{1+D_0M^2\beta^2\Delta L_{jj}(k,z)}. \tag{3.22}$$

In summary, we see that the result of deriving $F(k,t)$ from a more detailed description [$\nu=2$, i.e., Eqs. (3.8) and (3.9)] also leads, before introducing the overdamped limit, to explicit moment conditions for $m^{(1)}(k)$, $m^{(2)}(k)$, and $m^{(3)}(k)$, which were not revealed by the minimal description ($\nu=1$). The higher-order moments now depend on the moments of the higher-order memory function $\Delta L_{jj}(k,t)$. Also, the results generated from the more detailed description ($\nu=2$), allowed us to discuss the overdamped limit, although this only led us to rederive Ackerson's memory equation, including the explicit results for $m^{(0)}(k)$ and $m^{(1)}(k)$.

This inmediately suggests that going one step further, i.e., starting from a still more detailed description, should reveal additional features of the structure of $F(k,z)$ by expressing the memory function $\Delta L_{jj}(k,t)$ in terms of a higher-order memory function. In particular, we would expect that this procedure will lead to explicit expressions for additional moments of $F(k,t)$. Alarcon-Waess and Medina-Noyola [28] carried out this program precisely, by writing $\mathbf{a}(t)\equiv[\delta n(\mathbf{k},t),\delta j_l(\mathbf{k},t),\delta\sigma'(\mathbf{k},t)]$, with $\delta\sigma'(\mathbf{k},t)$ being defined by the momentum conservation equation [Eq. (3.11)], which can also be written as

$$\frac{\partial\delta j_l(\mathbf{k},t)}{\partial t}=-\frac{\zeta^0}{M}\delta j_l(\mathbf{k},t)+\frac{f^0(\mathbf{k},t)}{M}+ik\delta p(\mathbf{k},t)+ik\delta\sigma'(\mathbf{k},t), \tag{3.23}$$

with

$$\delta\sigma'(\mathbf{k},t)=-\delta p(\mathbf{k},t)+\delta\sigma^{zz}(\mathbf{k},t), \tag{3.24}$$

$p(k,t)$ being the Fourier transform of the local osmotic pressure $p(\mathbf{r},t)=p[n(\mathbf{r},t)]$, and $\delta\sigma^{zz}(k,t)$ being the instantaneous fluctuation of the isotropic diagonal component of the stress tensor

$$\sigma^{\alpha\beta}(\mathbf{k},t)\equiv\frac{1}{\sqrt{N}}\sum_{i=1}^{N}\left\{v_i^{\alpha}v_j^{\beta}-\frac{1}{2M}\sum_{j\neq i}\frac{r_{ij}^{\alpha}r_{ij}^{\beta}}{r_{ij}^2}P_k(r_{ij})\right\}e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}, \tag{3.25}$$

$$P_k(r_{ij})\equiv r_{ij}\frac{du(r_{ij})}{dr_{ij}}\,\frac{e^{i\mathbf{k}\cdot\mathbf{r}_{ij}(t)}-1}{\mathbf{k}\cdot\mathbf{r}_{ij}(t)}. \tag{3.26}$$

In these equations, $\mathbf{r}_{ij}\equiv\mathbf{r}_i-\mathbf{r}_j$, and $u(r_{ij})$ is the pair potential. The results of Alarcon-Waess and Medina-Noyola's exercise [28] is the following expression for $F(k,z)$:

$$F(k,z)=\frac{S(k)}{z+\dfrac{k^2D_0S^{-1}(\zeta^0/M)}{z+\dfrac{\zeta^0}{M}+\dfrac{k^2\chi_{\sigma\sigma}\chi_{jj}^{-1}}{z+\chi_{\sigma\sigma}^{-1}L_{\sigma\sigma}(k,z)}}}, \tag{3.27}$$

where [29]

$$\chi_{\sigma\sigma}(k)\equiv\frac{k_BT}{M^2}\left[3k_BT+n\int g(r)\frac{\partial^2u(r)}{\partial z^2}\left(\frac{1-\cos kz}{k^2}\right)d^3r\right]-\frac{1}{S(k)}\left(\frac{k_BT}{M}\right)^2. \tag{3.28}$$

From this equation, one can derive the moments $m^{(n)}(k)$ of $F(k,t)$. For $n=0$, 1, 2, and 3 one recovers the result in Eqs. (3.15)–(3.18), but now we also have explicit expressions for $m^{(4)}(k)$, namely,

$$m^{(4)}(k)=\frac{k^2}{M\beta}\left[\frac{k^2S^{-1}(k)}{M\beta}-\frac{\zeta^{02}}{M^2}+M\beta k^2\chi_{\sigma\sigma}(k)\right]. \tag{3.29}$$

For $n\geqslant 5$, $m^{(n)}(k)$ depends on the higher-order memory function $L_{\sigma\sigma}(k,z)$.

Let us now consider the overdamped limit, $z\ll z_B$, of Eq. (3.27). Neglecting z compared to z_B, just as we did to derive Eq. (3.19) from Eq. (3.14), leads to

$$F(k,z)=\frac{S(k)}{z+\cfrac{k^2D_0S^{-1}}{1+\cfrac{k^2D_0\chi_{\sigma\sigma}\chi_{jj}^{-2}}{z+\chi_{\sigma\sigma}^{-1}L_{\sigma\sigma}(k,z)}}}. \tag{3.30}$$

Once in the diffusive regime, this equation can be used to calculate the short-time moment conditions. As a result, we recover the expressions for $m^{(0)}(k)$ and $m^{(1)}(k)$ in Eqs. (3.20) and (3.21), which we derived from Eq. (3.19), but, in addition, we obtain an expression for the second moment, namely,

$$m^{(2)}(k)=3k^4D_0^2+nD_0\int d\mathbf{r}\,g(r)[1-\cos(\mathbf{k}\cdot\mathbf{r})]\times(\mathbf{k}\cdot\nabla)^2\beta u(r). \tag{3.31}$$

We now would like to see that this result for $m^{(2)}(k)$ coincides with Ackerson's result [Eq. (2.7)]. As it happens, it does not. The physical reason for this is certainly not obvious, but was correctly hinted at by Hess and Klein [12], who suggested that the static correlation $\chi_{\sigma\sigma}\equiv\langle\delta\sigma'(\mathbf{k})\delta\sigma'(-\mathbf{k})\rangle$ appearing in Eq. (3.27), should be replaced by the static correlation $\chi_{UU}\equiv\langle\delta\sigma_U'(\mathbf{k})\delta\sigma_U'(-\mathbf{k})\rangle$, where $\delta\sigma_U'(\mathbf{k})$ is the component of $\delta\sigma'(\mathbf{k},t)$ that depends only on the configurations, since the kinetic component $\delta\sigma_K'(\mathbf{k},t)$ of $\delta\sigma'(\mathbf{k},t)$ relaxes to equilibrium in the time scale τ_B. In fact, one can check that, if this replacement is made, the result for $m^{(2)}(k)$ would coincide with Ackerson's. However, this physical argument has not been expressed as a formal mathematical procedure which indeed leads to Eq. (3.30), with $\chi_{\sigma\sigma}(k)$ replaced by $\chi_{UU}(k)$. The notion of splitting $\delta\sigma'(\mathbf{k},t)$ in $\delta\sigma_U'(\mathbf{k},t)$ and $\delta\sigma_K'(\mathbf{k},t)$ can be formalized in a simple and explicit manner in the GLE formalism, and this is the subject of Sec. IV.

IV. KINETIC AND CONFIGURATIONAL COMPONENTS OF THE STRESS TENSOR

In Sec. III we illustrated the strategy of deriving expressions for $F(k,z)$ in terms of a hierarchy of memory functions. This strategy consisted of succesively enlarging the number ν of dynamics variables grouped in the vector $\mathbf{a}(t)$ of the noncontracted description represented by the GLE [Eq. (3.1)]. We illustrated this strategy by considering the nested sequence of levels: $\nu=1$, with $\mathbf{a}(t)=(\delta n(\mathbf{k},t))$; $\nu=2$, with $\mathbf{a}(t)=(\delta n(\mathbf{k},t),\delta j(\mathbf{k},t))$; and $\nu=3$, with $\mathbf{a}(t)=(\delta n(\mathbf{k},t),\delta j(\mathbf{k},t),\delta\sigma'(\mathbf{k},t))$. The underlying microscopic dynamics represented by the N-particle Langevin equation was assumed, and used explicitly [see the derivation of Eq. (3.11)]. In the absence of friction, these equations are just the equations describing the Newtonian dynamics of an atomic fluid [i.e., the solvent friction $\zeta^0=0$ in Eq. (2.1)]; this is a well-studied limit in the molecular hydrodynamic theory of fluids [2]. The results of Sec. III are thus correct and useful in this limiting regime, characterized by times $t\ll\tau_B=M/\beta$. Hess and Klein accurately pointed out that the stress tensor $\delta\sigma'(\mathbf{k},t)$ is a sum of two components, one of which depends only on the spatial configurations, and another which also depends on the particle's momenta. The latter exhibits more explicitly in its dynamic behavior the difference between short and long times, referred to the time scale τ_B. To see this, let us define $\delta\sigma_K'(\mathbf{k},t)$, the kinetic contribution of $\delta\sigma'(\mathbf{k},t)$, as [see eq. (3.25)]

$$\delta\sigma_K'(\mathbf{k},t)=\frac{1}{\sqrt{N}}\sum_{i=1}^{N}(v_i^z)^2e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}, \tag{4.1}$$

and let us also define $\sigma_U'(\mathbf{k},t)$ as the purely configurational component

$$\delta\sigma_U'(\mathbf{k},t)=-\frac{1}{2M\sqrt{N}}\sum_{i=1}^{N}\sum_{j\neq i}\frac{r_{ij}^{\alpha}r_{ij}^{\beta}}{r_{ij}^2}P_k(r_{ij})e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}-\delta p. \tag{4.2}$$

Clearly,

$$\delta\sigma'(\mathbf{k},t)=\delta\sigma_K'(\mathbf{k},t)+\delta\sigma_U'(\mathbf{k},t). \tag{4.3}$$

If we take the time derivative of Eq. (4.1), we have

$$\frac{\partial\delta\sigma_K'(\mathbf{k},t)}{\partial t}=\frac{1}{\sqrt{N}}\sum_{i=1}^{N}2v_i^z\dot{v}_i^ze^{i\mathbf{k}\cdot\mathbf{r}_i(t)}+\frac{ik}{\sqrt{N}}\sum_{i=1}^{N}(v_i^z)^3e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}. \tag{4.4}$$

If we now use the microscopic dynamics presented by the N-particle Langevin equation [Eq. (2.1)], we can write Eq. (4.4) as

$$\frac{\partial\delta\sigma_K'(\mathbf{k},t)}{\partial t}=\frac{-2\zeta^0}{M}\delta\sigma_K'(k,t)+\varphi(k,t)+\frac{1}{\sqrt{N}}\sum_{i=1}^{N}2v_i^z\dot{v}_iF_i^ze^{i\mathbf{k}\cdot\mathbf{r}_i(t)}+\frac{ik}{\sqrt{N}}\sum_{i=1}^{N}(v_i^z)^3e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}. \tag{4.5}$$

This form of writing the relaxation equation for $\delta\sigma_K'(k,t)$ is analogous to Eq. (3.11) for $\delta j_l(\mathbf{k},t)$. The first term or the right-hand side of this equation clearly exhibits the fact that the time derivative of $\delta\sigma_K'(t)$ couples with $\delta\sigma_K'(t)$ itself through a dissipative frictional term, with a decay constant $\tau_B/2$.

In contrast, if we take the time derivative of $\delta\sigma_U'(\mathbf{k},t)$ in Eq. (4.2), the absence of an explicit dependence of $\delta\sigma_U'(\mathbf{k},t)$ on the particles' velocities prevents the possibility of a rapid decay of the type exhibited by the first term on the right-hand side of Eq. (4.5) for $\delta\sigma_K'(\mathbf{k},t)$. Thus these two components of the stress tensor $\delta\sigma'(\mathbf{k},t)$ clearly have a qualitatively different dynamic character in the diffusive regime of Brownian fluids, and this suggests that we should treat them separately. In the absence of friction, i.e., for atomic fluids, this qualitative difference does not exist, and, hence, we can combine $\delta\sigma_K'(\mathbf{k},t)$ and $\delta\sigma_U'(\mathbf{k},t)$ into a single variable $\delta\sigma'(\mathbf{k},t)$ with no important consequences. However, if friction is present, and we want to be prepared to take eventually the overdamped limit, we better take into account this qualitative difference between $\delta\sigma_K'(\mathbf{k},t)$ and $\delta\sigma_U'(\mathbf{k},t)$ right at the outset. The GLE formalism provides the obvious and natural manner of doing this, namely, to include both $\delta\sigma'_K(\mathbf{k},t)$ and $\delta\sigma'_U(\mathbf{k},t)$ as independent variables in the uncontracted description $\mathbf{a}(t)$.

Thus let us now consider the description of the collective dynamics of a Brownian fluid in terms of the vector $\mathbf{a}(t) \equiv (\delta n(\mathbf{k},t), \delta j(\mathbf{k},t), \delta\sigma'_K(\mathbf{k},t), \delta\sigma'_U(\mathbf{k},t))$. The first step in this procedure is to make sure that an important requirement of the components of $\mathbf{a}(t)$ is being satisfied by the new variables $\delta\sigma'_K(\mathbf{k},t)$ and $\delta\sigma'_U(\mathbf{k},t)$. This refers to the requirement of static uncorrelation between the components $a_i(t)$ $(i=1,2,\ldots,\nu)$, i.e., to the diagonality of the static correlation matrix $\chi = \langle \mathbf{a}(0)\mathbf{a}^T(0)\rangle$. Using the microscopic definitions [Eqs. (3.4), (3.6), (4.1), and (4.2)] of the components of $\mathbf{a}(t)$, one can perform the statistical mechanical calculation of the correlation matrix χ. From the result of such an exercise, we realize that, with this choice of variables, χ does not happen to be diagonal.

The required diagonalization, however, is easily achieved by means of a change of variable leading to the following redefinition of $\mathbf{a}(t)$.

$$\mathbf{a}(t) \equiv [\delta n(\mathbf{k},t), \delta j(\mathbf{k},t), \delta\sigma_K(\mathbf{k},t), \delta\sigma_U(\mathbf{k},t)], \tag{4.6}$$

with

$$\delta\sigma_K(\mathbf{k},t) \equiv \delta\sigma'_K(\mathbf{k},t) - \chi_{jj}\delta n(\mathbf{k},t), \tag{4.7}$$

$$\delta\sigma_U(\mathbf{k},t) \equiv \delta\sigma'_U(\mathbf{k},t) + \chi_{jj}\delta n(\mathbf{k},t). \tag{4.8}$$

Although rather lengthy [30], the equilibrium statistical mechanical calculation of the new static correlation function is straighforward. The result can be written as

$$\chi = \begin{bmatrix} \chi_{nn} & 0 & 0 & 0 \\ 0 & \chi_{jj} & 0 & 0 \\ 0 & 0 & \chi_{KK} & 0 \\ 0 & 0 & 0 & \chi_{UU} \end{bmatrix}, \tag{4.9}$$

with $\chi_{nn} = S(k)$ and $\chi_{jj} = k_B T/M$, as before, and with χ_{KK} and χ_{UU} given by

$$\chi_{KK} = 2\chi_{jj}^2,$$

$$\chi_{UU} = \chi_{jj}^2 \left[1 + n \int d\mathbf{r}\, g(r) \frac{\partial^2 \beta u(r)}{\partial z^2} \left(\frac{1-\cos(kz)}{k^2} \right) - \frac{1}{S(k)} \right]. \tag{4.10}$$

Now we are ready to write the generalized Langevin equation in the format of Eq. (3.1) for our new vector $\mathbf{a}(t)$ of Eq. (4.6). Let us first note that all the variables, except $a_2(t) = \delta j_l(\mathbf{k},t)$ are even functions under time reversal. According to Onsager reciprocity relations, and the general anti-Hermiticity of ω and Hermiticity of $L(z)$[14], we have that the only possibly nonzero elements of the matrix ω and $L(z)$ are

$$\omega = \begin{bmatrix} 0 & \omega_{nj} & 0 & 0 \\ -\omega^*_{nj} & 0 & \omega_{jK} & \omega_{jU} \\ 0 & -\omega^*_{jK} & 0 & 0 \\ 0 & -\omega^*_{jU} & 0 & 0 \end{bmatrix}, \tag{4.11}$$

$$L(t) = \begin{bmatrix} L_{nn} & 0 & L_{nK} & L_{nU} \\ 0 & L_{jj} & 0 & 0 \\ L^*_{nK} & 0 & L_{KK} & L_{KU} \\ L^*_{nU} & 0 & L^*_{KU} & L_{UU} \end{bmatrix}. \tag{4.12}$$

The determination of the nonzero elements of ω and of some of the nonzero elements of $L(t)$ is rather straightforward, since, from the exact continuity equation,

$$\frac{\partial \delta n(\mathbf{k},t)}{\partial t} = ik\,\delta j_l(\mathbf{k},t), \tag{4.13}$$

we immediately see that $\omega_{nj} = -ik\chi_{jj}$, and that $L_{nn} = L_{nK} = L_{nU} = 0$. Similarly, from Eq. (3.23), which can be rewritten as

$$\frac{\partial \delta j_l(\mathbf{k},t)}{\partial t} = -\frac{\zeta^0}{M}\delta j_l(\mathbf{k},t) + \frac{1}{M} f^0(\mathbf{k},t) + ik\,\delta p(\mathbf{k},t) + ik\,\delta\sigma_K(\mathbf{k},t) + ik\,\delta\sigma_U(\mathbf{k},t), \tag{4.14}$$

we can see that $\omega_{jK}\chi_{jU}^{-1} = \omega_{jU}\chi_{UU}^{-1} = -ik$ and $L_{jj}\chi_{jj}^{-1} = \zeta^0/M$. As a result, all the elements of the ''frequency'' matrix ω have been determined, and in fact, only the kinematic coefficients $L_{KK}(k,z)$, $L_{KU}(k,z) = L_{UK}(k,z)$, and $L_{UU}(k,z)$ remain undetermined by general symmetry principles, or physical principles such as mass or momentum conservation. Thus the time-evolution equations that complete the noncontracted description for the components of the vector $\mathbf{a}(t)$ in Eq. (4.6) are the mass and momentum conservation equations [Eqs. (4.13) and (4.14)], along with the following equations for $\delta\sigma_K(\mathbf{k},t)$ and $\delta\sigma_U(\mathbf{k},t)$:

$$\begin{aligned} \frac{\partial \delta\sigma_K(\mathbf{k},t)}{\partial t} = {} & ik\chi_{KK}\chi_{jj}^{-1}\delta j_l(\mathbf{k},t) \\ & - \int_0^t L_{KK}(\mathbf{k},t-t')\chi_{KK}^{-1}\delta\sigma_K(\mathbf{k},t)dt' \\ & - \int_0^t L_{UK}(\mathbf{k},t-t')\chi_{UU}^{-1}\delta\sigma_U(\mathbf{k},t)dt' + f_K(\mathbf{k},t), \end{aligned} \tag{4.15}$$

$$\begin{aligned} \frac{\partial \delta\sigma_U(\mathbf{k},t)}{\partial t} = {} & ik\chi_{UU}\chi_{jj}^{-1}\delta j_l(\mathbf{k},t) \\ & - \int_0^t L_{UU}(\mathbf{k},t-t')\chi_{UU}^{-1}\delta\sigma_U(\mathbf{k},t)dt' \\ & - \int_0^t L_{UK}(\mathbf{k},t-t')\chi_{KK}^{-1}\delta\sigma_K(\mathbf{k},t)dt' + f_U(\mathbf{k},t). \end{aligned} \tag{4.16}$$

In these equations, only $L_{KK}(\mathbf{k},t)$, $L_{UU}(\mathbf{k},t)$, and $L_{UK}(\mathbf{k},t)$ remain unknown.

From this extended dynamic description [Eqs. (4.13)–(4.16)], we can derive the time-evolution equation for $\delta n(\mathbf{k},t)$. It is not difficult to show, using Eqs. (4.13)–(4.16), along with the contraction theorem, that such an equation reads

$$\frac{\partial \delta n(\mathbf{k},t)}{\partial t} = -\int_0^t L(k,t-t')\chi_{nn}^{-1}\delta n(\mathbf{k},t')dt' + f(\mathbf{k},t), \tag{4.17}$$

where $f(\mathbf{k},t)$ is a random term with zero mean and time-dependent correlation function $\langle f(\mathbf{k},0)f(-\mathbf{k},0)\rangle = L(k,t)$ with $L(k,t)$ given, in Laplace space, by

$$L(k,z) = \frac{k^2\chi_{jj}}{z + z_B + \chi_{jj}^{-1}\Delta L_{jj}(k,z)}, \tag{4.18}$$

with

$$\Delta L_{jj}(k,z) = \frac{k^2\chi_{KK}}{z + L_{KK}\chi_{KK}^{-1}} + \frac{k^2\chi_{UU}\left[1 - \dfrac{L_{KU}\chi_{UU}^{-1}}{z + L_{KK}\chi_{KK}^{-1}}\right]^2}{z + L_{UU}\chi_{UU}^{-1} - \dfrac{\chi_{KK}^{-1}L_{KU}L_{UK}\chi_{UU}^{-1}}{z + L_{KK}\chi_{KK}^{-1}}}. \tag{4.19}$$

Equations (4.17) and (4.18) correspond to Eqs. (3.2), (3.10), and (3.13) of Sec. III, which are now complemented by the explicit expression in Eq. (4.19) for $\Delta L_{jj}(k,z)$ in terms of the higher-order memory functions $L_{KK}(k,z)$, $L_{UU}(k,z)$, and $L_{KU}(k,z)$. In fact, let us finally summarize these results as an explicit expression for the collective dynamic structure factor $F(k,z)$ in terms of these memory functions, namely,

$$F(k,z) = \cfrac{S(k)}{z + \cfrac{k^2S^{-1}(k)\chi_{jj}}{z + z_B + \cfrac{k^2\chi_{jj}^{-1}\chi_{KK}}{z + L_{KK}\chi_{KK}^{-1}} + \cfrac{k^2\chi_{jj}^{-1}\chi_{UU}\left[1 - \dfrac{L_{KU}\chi_{UU}^{-1}}{z + L_{KK}\chi_{KK}^{-1}}\right]^2}{z + L_{UU}\chi_{UU}^{-1} - \dfrac{\chi_{KK}^{-1}L_{KU}L_{UK}\chi_{UU}^{-1}}{z + L_{KK}\chi_{KK}^{-1}}}}}. \tag{4.20}$$

It is not difficult to show that the moment conditions up to $m^{(4)}(k)$, that result from Eq. (4.20), are again given by the results in Eqs. (3.15)–(3.18) and (3.29) of Sec. III, whereas $m^{(n)}(k)$, for $n>4$, depends on the memory functions $L_{UU}(k,z)$, $L_{KK}(k,z)$, and $L_{KU}(k,z)$. Thus, with respect to these short-time conditions, augmenting the noncontracted description from $\mathbf{a}(t) \equiv (\delta n(\mathbf{k},t), \delta j_l(\mathbf{k},t), \delta\sigma(\mathbf{k},t))$ to $\mathbf{a}(t) \equiv [\delta n(\mathbf{k},t), \delta j_l(\mathbf{k},t), \delta\sigma_K(\mathbf{k},t), \delta\sigma_U(\mathbf{k},t)]$ did not lead to any new information. It is only in the overdamped limit, which is our present interest, when the results in Eq. (4.20) turn out to be particularly useful.

To see this, let us rewrite Eq. (4.20) in a slightly different manner, in preparation to taking the overdamped limit $z/z_B \ll 1$:

$$F(k,z) = \cfrac{S(k)}{z + \cfrac{k^2D_0S^{-1}(k)}{1 + \dfrac{z}{z_B} + \cfrac{k^2D_0\chi_{KK}}{z + L_{KK}\chi_{KK}^{-1}} + \cfrac{k^2D_0\chi_{UU}\left[1 - \dfrac{L_{KU}\chi_{UU}^{-1}}{z + L_{KK}\chi_{KK}^{-1}}\right]^2}{z + L_{UU}\chi_{UU}^{-1} - \dfrac{\chi_{KK}^{-1}L_{KU}L_{UK}\chi_{UU}^{-1}}{z + L_{KK}\chi_{KK}^{-1}}}}}. \tag{4.21}$$

In this equation, we have an obvious and explicit dependence on z/z_B which can inmediately be neglected. However, an additional dependence of $F(k,z)$ on z/z_B could be hidden in the memory functions $L_{UU}(k,z)$, $L_{KK}(k,z)$, and $L_{KU}(k,z)$, and this requires a more careful discusion. Unfortunately, the present theoretical approach does not allow any further determination of those memory functions based on exact and general symmetry principles. However, we have not yet used the fact that there is a strong dynamic asymmetry between the variables $\delta\sigma_K(\mathbf{k},t)$ and $\delta\sigma_U(\mathbf{k},t)$, as discussed at the begining of this section. In fact, in Eq. (4.5) we showed explicitly that the kinetic contribution $\delta\sigma'_K(\mathbf{k},t)$ of the stress tensor must relax initially with an exponential decay with relaxation time $\tau_B/2$. In contrast, no similar relaxation can be argued for $\delta\sigma'_U(\mathbf{k},t)$, since this variable does not depend on the velocities of the Brownian particles. Although in order to diagonalize χ we still transformed from $\delta\sigma'_K(\mathbf{k},t)$ and $\delta\sigma'_U(\mathbf{k},t)$ to $\delta\sigma_K(\mathbf{k},t)$ and $\delta\sigma_U(\mathbf{k},t)$, the new variables $\delta\sigma_K(\mathbf{k},t)$ and $\delta\sigma_U(\mathbf{k},t)$ should still retain this fundamental dynamic asymmetry; that is, $\delta\sigma_K(\mathbf{k},t)$ carries the dependence on the particle's velocities, and $\delta\sigma_U(\mathbf{k},t)$ continues to be a purely configurational variable. Thus it is perfectly reasonable to assume that the relaxation of $\delta\sigma_K(\mathbf{k},t)$ does have a fast exponential component with a relaxation time $\tau_B/2$, and that $\delta\sigma_U(\mathbf{k},t)$ does not. Mathematically, this can be expressed by the assumption that neither $L_{UU}(k,z)$ or $L_{KU}(k,z)$ has a dominant term proportional to z_B, but that $L_{KK}(k,z)$ does, i.e., that, to first approximation, $L_{KK}(k,z)$ should be written as

$$L_{KK}(k,z)=2z_B+\Delta L_{KK}(k,z), \tag{4.22}$$

with $\Delta L_{KK}(k,z)$ being a function that does not scale linearly with z_B, i.e., that

$$\lim_{\frac{z}{z_B}\to 0} L_{KK}(k,z)=\lim_{\frac{z}{z_B}\to 0} 2z_B\left[1+\frac{\Delta L_{KK}(k,z)}{2z_B}\right]\approx 2z_B. \tag{4.23}$$

Similarly, we shall assume that $L_{UU}(k,z)/z_B$ and $L_{UK}(k,z)/z_B$ will vanish in the same limit. With these considerations, it is now easy to see that the rather complex expression for $F(k,z)$ in Eq. (4.20) will reduce, in the overdamped limit, to the following surprisingly simple expression:

$$F(k,z)=\cfrac{S(k)}{z+\cfrac{k^2D_0S^{-1}}{1+\cfrac{k^2D_0\chi_{UU}\chi_{jj}^{-2}}{z+\chi_{UU}^{-1}L_{UU}(k,z)}}}. \tag{4.24}$$

As it happens, this result is almost identical to that obtained from the noncontracted description defined by $\mathbf{a}(t)\equiv(\delta n(\mathbf{k},t),\delta j_l(\mathbf{k},t),\delta\sigma(\mathbf{k},t))$, i.e., Eq. (3.30) of Sec. III. The main difference now is the appearance of $\chi_{UU}(k)$ and $L_{UU}(k,z)$ in Eq. (4.24), instead, respectively, of $\chi_{\sigma\sigma}(k)$ and $L_{\sigma\sigma}(k,z)$ appearing in Eq. (3.29).

Once in the diffusive regime, described by Eq. (4.24), we can discuss the short-time behavior of $F(k,t)$ in terms of its moment conditions. It is not difficult to show, from Eq. (4.24), that $m^{(n)}(k)$ are given by

$$m^{(0)}(k)=S(k), \tag{4.25}$$

$$m^{(1)}(k)=-k^2D_0, \tag{4.26}$$

$$m^{(2)}(k)=k^4D_0^2+nD_0\int d\mathbf{r}\,g(r)[1-\cos(\mathbf{k}\cdot\mathbf{r})] \times(\mathbf{k}\cdot\boldsymbol{\nabla})^2\beta u(r), \tag{4.27}$$

whereas the higher-order moments depend on $L_{UU}(k,z)$. At this point, we note that the second moment $m^{(2)}(k)$ thus obtained, unlike that in Eq. (3.30) of Sect. II, does coincide with Ackerson's result in Eq. (2.7). As already emphasized, Ackerson derived this result directly from the previously-overdamped microscopic dynamics represented by the N-particle Smoluchowski equation. Thus, although no formal proof is available that this strategy and the present one should lead to strictly the same short-time moment conditions, the consistency between both approaches is reassuring. Of course, one could think of deriving higher-order moment conditions by developing a similar exercise to the one carried out in this section, i.e., by including additional variables in the noncontracted description. This, however, is certainly not the aim of our present work, since Ackerson's approach [6] is, for this purpose, much more straightforward [for example, the corresponding result for the third moment, Eq. (2.8), was obtained [19] as a straightforward extension of Ackerson's calculation]. Our aim in this paper, instead, is to develop an expression for the full time dependence of $F(k,t)$, in terms of higher-order memory functions, on which we could make the least harmful approximations. With this purpose in mind, the availability of additional moment conditions obtained directly from the Smoluchowski equation, could in fact be used as a guideline to reveal more details of the structure of the memory function $L_{UU}(k,z)$, which our methodology has left undetermined. To illustrate this, let us start from our general expression for $F(k,t)$ in Eq. (4.24), to calculate the third moment $m^{(3)}(k)$. For this, we have to make assumptions about the analytic properties of $L_{UU}(k,t)$ at short times. If we naively assume that $L_{UU}(k,t)$ is an analytic function at $t=0$, and expand in a Taylor series, the result that we would obtain for $m^{(3)}(k)$ happens to be different from the Smoluchowski result in Eq. (2.8). Thus we can use this observation to revise such an analytic ansatz for $L_{UU}(k,t)$, and assume a more general functional dependence.

For example, let us admit that $L_{UU}(k,t)$ may have a ''Markovian'' contribution, of the type $L^0(k)2\delta(t)$, plus an analytic term that we denote as $\Delta L_{UU}(k,t)$, i.e.,

$$L_{UU}(k,t)=L^0(k)2\delta(t)+\Delta L_{UU}(k,t)=L^0(k)2\delta(t) +\sum_{n=0}^{\infty}\frac{L^{(n+1)}(k)t^n}{n!}, \tag{4.28}$$

or, in Laplace space,

$$L_{UU}(k,z)=\sum_{n=0}^{\infty}\frac{L^{(n)}(k)}{z^n}. \tag{4.29}$$

Using this assumption in Eq. (4.24), we can derive the following result for $m^{(3)}(k)$:

$$\begin{aligned}m^{(3)}(k)={}&-2k^6D_0^3M^2\beta^2\chi_{UU}(k)S^{-1}(k)\\&-k^6D_0^3M^4\beta^4\chi_{UU}^2(k)-k^6D_0^3S^{-2}(k)\\&-k^4D_0^2M^2\beta^2\chi_{UU}(k)L^{(0)}(k).\end{aligned} \tag{4.30}$$

It is not difficult to see, using Eq. (4.10) for $\chi_{UU}(k)$, that if $L^0(k)=0$, this result for $m^{(3)}(k)$ cannot be reconciled with the Smoluchowski result in Eq. (2.8). If, in contrast, we assume that $L^{(0)}(k)\neq 0$, and require that the two results coincide, then we have to force the equality of the right-hand sides of Eqs. (4.30) and (2.8), thus leading to a condition that determines the otherwise unknown parameter $L^{(0)}(k)$. This results in the following explicit expression for $L^{(0)}(k)$ in terms of purely static quantities:

$$
\begin{aligned}
M^2\beta^2L^0(k)={}&n\int d^3r\, g(r)\,\frac{\partial^2\beta u(r)}{\partial z^2}[1+2\cos kz]\\
&-\frac{D_0n^2}{k^2}\left[\int d^3r\, g(r)\,\frac{\partial^2\beta u(r)}{\partial z^2}(1-\cos kz)\right]^2\\
&+\frac{2D_0n}{k}\left[\int d^3r\, g(r)\,\frac{\partial^3\beta u(r)}{\partial z^3}\sin kz\right]^2\\
&+\frac{2D_0n}{k^2}\int d^3r\, g(r)(1-\cos kz)\left[\frac{\partial\boldsymbol{\nabla}\beta u(r)}{\partial z}\right]^2\\
&+\frac{D_0n^2}{k^2}\int d^3r\, d^3r'\, g(\mathbf{r},\mathbf{r}')(1-2\cos kz\\
&+\cos[k(z-z')])\left[\frac{\partial\boldsymbol{\nabla}\beta u(r)}{\partial z}\right]\cdot\left[\frac{\partial\boldsymbol{\nabla}'\beta u(r')}{\partial z'}\right].
\end{aligned}
\tag{4.31}
$$

From now on, we indeed adopt this condition as the determination of $L^0(k)$. As a result, we arrive at the following final expression for $F(k,z)$:

$$
F(k,z)=\cfrac{S(k)}{z+\cfrac{k^2D_0S^{-1}}{1+\cfrac{k^2D_0\chi_{UU}\chi_{jj}^{-2}}{z+\chi_{UU}^{-1}L^0(k)+\chi_{UU}^{-1}\Delta L_{UU}(k,z)}}},
\tag{4.32}
$$

which then expresses $F(k,z)$ in terms only of static quantities, and of the non-Markovian memory function $\Delta L_{UU}(k,z)$. The idea is that this expression for $F(k,z)$ should be suitable for the proposal of simple approximations at the level of $\Delta L_{UU}(k,z)$.

At this point, let us mention that exactly the same analysis that we have carried out so far for $F(k,z)$ can be extended to the self-intermediate scattering function $F_S(k,z) \equiv\langle e^{i\mathbf{k}\cdot\Delta\mathbf{R}(t)}\rangle$, where $\Delta\mathbf{R}(t)=\mathbf{R}(t)-\mathbf{R}(0)$ is the displacement of a tagged particle during a time *t*. For this, we have to repeat all the steps and arguments starting from Sec III, but considering the dynamic variable $n_S(\mathbf{k},t)\equiv e^{i\mathbf{k}\cdot\mathbf{R}(t)}$ instead of the collective variable $n(\mathbf{k},t)$ of Eq. (3.4). Omiting the details, we can summarize the results of such derivation in the following general expression for $F_S(k,z)$,

$$
F_S(k,z)=\cfrac{1}{z+\cfrac{k^2D_0}{1+\cfrac{k^2D_0\chi_{UU}^{(S)}(k)\chi_{jj}^{-2}}{z+\chi_{UU}^{(S)-1}(k)L_S^0(k)+\chi_{UU}^{(S)-1}\Delta L_{UU}^{(S)}(k,z)}}},
\tag{4.33}
$$

where

$$
\chi_{UU}^{(S)}(k)\equiv\frac{\chi_{jj}^2}{k^2}\left[n\int d\mathbf{r}\, g(r)\,\frac{\partial^2\beta u(r)}{\partial z^2}\right]
\tag{4.34}
$$

and

$$
\begin{aligned}
D_0M^2\beta^2L_S^0(k)\equiv{}&k^2D_0^2\left[n\int d\mathbf{r}\, g(r)\,\frac{\partial^2\beta u(r)}{\partial z^2}\right]\\
&-D_0^2n^2\left[\int d^3r\, g(r)\,\frac{\partial^2\beta u(r)}{\partial z^2}\right]^2\\
&+2D_0^2n\int d^3r\, g(r)\left[\frac{\partial\boldsymbol{\nabla}\beta u(r)}{\partial z}\right]^2\\
&+D_0^2n^2\int d^3r\, d^3r'\, g(\mathbf{r},\mathbf{r}')\\
&\times\left[\frac{\partial\boldsymbol{\nabla}\beta u(r)}{\partial z}\right]\cdot\left[\frac{\partial\boldsymbol{\nabla}'\beta u(r')}{\partial z'}\right].
\end{aligned}
\tag{4.35}
$$

Equations (4.32) and (4.33) are the most general results of this work. They write $F(k,z)$ and $F_S(k,z)$, in terms only of their respective unknown memory funcion $\Delta L_{UU}(k,z)$ and $\Delta L_{UU}^{(S)}(k,z)$ (recall that all the other elements entering in these equations are well-defined static properties, which we assume to be previously determined). Of course, we could still explore further levels of the hierarchical use of the GLE formalism, so as to investigate some exact features of these unknown higher-order memory function. At this point, however, we want to consider possible strategies for their approximate determination. The simplest of them is, of course, to neglect these unknown memory functions. If we set $\Delta L_{UU}(k,z)=0$ in Eq. (4.32), we obtain a closed analytic approximation for $F(k,z)$, namely,

$$
F(k,z)=\cfrac{S(k)}{z+\cfrac{k^2D_0S^{-1}}{1+\cfrac{k^2D_0\chi_{UU}\chi_{jj}^{-2}}{z+\chi_{UU}^{-1}L^0(k)}}}.
\tag{4.36}
$$

This approximation yields the exact (i.e., the Smoluchowski) values for the moments $m^{(0)}(k)$, $m^{(1)}(k)$, and $m^{(2)}(k)$, and, by construction [due to Eq. (4.31)] also for $m^{(3)}(k)$. In fact, one can show that this approximation coincides exactly with the so-called single-exponential memory (SEXP) approximation [19]. As it turns out, this simple approximation for $F(k,z)$ already happens to be reasonably accurate in the short-time regime, and even at intermediate times.

The self-diffusion version of the SEXP approximation is obtained from Eq. (4.33) when we set $\Delta L_{UU}^{(S)}(k,z)=0$. As stated above, this has proved to be the simplest, yet practical, approximation to be employed in the interpretation of experimental or simulated self-diffusion properties of colloidal suspensions. Our current interest is to extend these applications to collective diffusion, simultaneously attempting to go beyond the SEXP approximation, as we suggest in Sec. V.

V. CONCLUSIONS

In this paper we have addressed one particular aspect of the theory of colloid dynamics, namely, the formal procedure for taking the overdamped limit in the general expression for $F(k,t)$ and $F_S(k,t)$ derived from the microscopic dynamics represented by the N-particle Langevin equation. This led us to our main results, namely, the expressions for $F(k,t)$ and $F_S(k,t)$ in Eqs. (4.32) and (4.33) above, valid in the diffusive (or overdamped) regime. These expressions write $F(k,t)$ and $F_S(k,t)$ in terms only of static structural properties and of the memory function $\Delta L_{UU}(k,z)$ and $\Delta L_{UU}^{(S)}(k,z)$, respectively. The present exercise leaves these memory functions undetermined. However, we expect that, at least for short and intermediate times, simple approximations for $\Delta L_{UU}(k,z)$ and $\Delta L_{UU}^{(S)}(k,z)$ can be devised, which will lead to fairly accurate approximations for $F(k,t)$ and $F_S(k,t)$. We already mentioned that the most trivial assumption, $\Delta L_{UU}(k,z)=\Delta L_{UU}^{(S)}(k,z)=0$, corresponds to one of the most widely used approximate schemes in colloid dynamics namely, the SEXP approximation. This scheme is oriented, by construction, to describe the dynamic properties in the short- and intermediate-time regimes, which can be most easily probed by dynamic light scattering experiments or Brownian dynamics simulations. Under some circumstances, however, the asymptotically long-time behavior of the system becomes particularly important, as happens for highly dense fluids near, for example, their glass transition. In order to describe the main dynamic features of such highly correlated colloidal fluids, we have to go beyond the SEXP approximation. The results in Eqs. (4.32) and (4.33) will prove particularly useful in this regard. In fact, in separate communications [31,32], we shall present a more elaborate approximate scheme, far beyond the SEXP approximation, which amounts to the proposal of approximations at the level of $\Delta L_{UU}(k,z)$ and $\Delta L_{UU}^{(S)}(k,z)$. Such a scheme ends up expressing these memory functions in terms of the $F(k,t)$ and $F_S(k,t)$ themselves, thus defining a fully self-consistent scheme bearing a strong similarity to the self-consistent theories constructed using a mode-mode coupling anzatz [9,33]. Our proposal, however, will be based on the formalization of two physically intuitive notions. The first is the expectation that collective dynamics should be simply related to self-dynamics, in the spirit of Vineyard's approximation [1,2,34]. The second consists of the expectation that $F_S(k,t)$ should be simply related to the k-independent properties which describe the Brownian motion of a tagged particle. The simplest, well-known ansatz is the Gaussian approximation $F_S(k,t)=e^{-k^2W(t)}$, where $W(t)$ is the mean squared displacement of a tagged particle. Our results in Eq. (4.33), however, suggest alternative methods. The detailed explanation of the resulting self-consistent scheme, and of its concrete applications, will be provided separately [32]. Here we decided to focus on the most formal and rigorous aspects of the construction of this self-consistent theory, because of their intrinsic interest, and so as to have a simple reference for future extensions to more complex conditions, such as the consideration of colloidal mixtures or the treatment of hydrodynamic interactions.

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