

## Self-consistent generalized Langevin equation for colloidal mixtures

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A self-consistent theory of collective and tracer diffusion in colloidal mixtures is presented. This theory is based on exact results for the partial intermediate scattering functions derived within the framework of the generalized Langevin equation formalism, plus a number of conceptually simple and sensible approximations. The first of these consists of a Vineyard-like approximation between collective and tracer diffusion, which writes the collective dynamics in terms of the memory function related to tracer diffusion. The second consists of interpolating this only unknown memory function between its two exact limits at small and large wave vectors; for this, a phenomenologically determined, but not arbitrary, interpolating function is introduced: a Lorentzian with its inflection point located at the first minimum of the partial static structure factor. The small wave-vector exact limit involves a time-dependent friction function, for which we take a general approximate result, previously derived within the generalized Langevin equation formalism. This general result expresses the time-dependent friction function in terms of the partial intermediate scattering functions, thus closing the system of equations into a fully self-consistent scheme. This extends to mixtures a recently proposed self-consistent theory developed for monodisperse suspensions [Yeomans-Reyna and Medina-Noyola, *Phys. Rev. E* **64**, 066114 (2001)]. As an illustration of its quantitative accuracy, its application to a simple model of a binary dispersion in the absence of hydrodynamic interactions is reported.

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### I. INTRODUCTION

The characterization of the dynamic properties of colloidal *mixtures* is an important subject, due to the fact that monodispersity is only an idealized limit, rarely encountered under practical conditions. Many industrial and natural processes involve colloidal systems in which the deviations from monodispersity are precisely the source of their characteristic dynamic and rheological behavior [1–3]. The fundamental understanding of the dynamics of colloids has been facilitated, however, by the systematic experimental, theoretical, and simulation modeling of monodisperse systems [4–7]. Advances have been made in extending some of these studies to colloidal mixtures from the experimental [1,2,8] and from the theoretical [9–11] points of view. Still, the systematic extension and application to colloidal mixtures of most of the approaches that proved successful in the monodisperse case still remains as a relevant and challenging subject [7].

Among the few theoretical proposals devised to describe the intermediate- and long-time properties of colloidal mixtures of experimental interest, we have the so-called single exponential memory (SEXP) approximation [10]. This approximation, however, has been employed mostly in the interpretation of *tracer-diffusion* experiments or simulations in bidisperse colloidal suspensions of highly interacting particles [8,12,13]. For collective dynamics, it has only been applied in the case of monodisperse systems [14,15], except for the application to mixtures in our recent and closely related paper [16]. Although its validity is only guaranteed at short times, the SEXP approximation should provide a useful

and simple first-order description of the collective properties of colloidal mixtures in this regime [7,10].

On the other hand, two more robust self-consistent schemes are available in the literature, capable of providing an accurate description of the self- and collective-dynamic properties of a colloidal dispersion at intermediate and long times. The mode-coupling self-consistent scheme developed by Nägele *et al.* [11,17,18] has been extensively applied to the description of important dynamic phenomena and conditions. Such a scheme has also been extended and applied in various directions, one of them involving precisely colloidal mixtures [11]. So far this is the theoretical scheme that has been applied more thoroughly to collective diffusion in mixtures, although important issues still remain to be addressed with this or other approaches.

An alternative proposal of a self-consistent approximate theory of colloid dynamics has recently been developed [19–21] and applied to monodisperse model colloidal systems [22]. This theory is based on the generalized Langevin equation (GLE) formalism and on the concept of contraction of the description [23], which leads to exact expressions for the (self- and collective-) intermediate scattering functions of a colloidal dispersion in terms of the corresponding unknown memory functions. These exact expressions must be complemented with a number of approximations, leading to a closed system of equations that has to be solved self-consistently. One of the main advantages of this theory is the fact that it incorporates the exact short-time limiting behavior. The specific applications of this scheme to describe collective-diffusion properties, however, have only referred to monodisperse systems [22]. Given its high level of accuracy in

such applications, it is desirable to attempt its extension to the context of colloidal mixtures. The main aim of the present paper is precisely to provide such an extension.

The present theory is based on recently derived [16] exact memory-function expressions for the partial intermediate scattering functions of a colloidal mixture. These general results can be derived through a number of methods, such as the projection operator method employed by Nägele *et al.* [11], or the generalized Langevin equation approach [19,23]. Here we shall refer to the latter, since its hierarchical structure allows its systematic application to yield increasingly more detailed information on the properties of the hierarchy of memory functions [16]. As in the monodisperse case [21], these exact results are then complemented with a number of conceptually simple approximations. The first consists of Vineyard-like approximations between collective and tracer diffusion, established at the level of higher-order memory functions [20]. These relations write both, collective and tracer dynamics, in terms of a single unknown memory function, namely, that related to tracer diffusion. The second approximation consists of the interpolation of this unknown memory function between its two exact limits at small and large wave vectors; for this, we introduced a phenomenologically determined, but not arbitrary, interpolating Lorentzian function with its inflection point located at the first minimum (beyond the main peak) of the partial static structure factor. The small wave-vector limit involves a time-dependent friction function, for which we take a general approximate result, previously derived within the generalized Langevin equation formalism [23,24]. This general result expresses the time-dependent friction function in terms of the partial intermediate scattering functions, thus closing the system of equations into a fully self-consistent scheme.

Let us mention the main limitations of the theory presented in this paper. First of all, in this first account we do not consider hydrodynamic interactions. Although these constitute particularly important effects in colloid dynamics, our approach can only incorporate them through some form of hydrodynamic renormalization of the short-time self-diffusion properties of the corresponding system in the absence of hydrodynamic interactions [2,25]. Similarly, due to the incorporation of exact short-time conditions, which involve the restriction to continuous pairwise interactions, the theory is not directly applicable to hard-sphere potentials. Here, again, one can attempt to use the dynamical equivalence between hard- and soft-core potentials [26] to circumvent this limitation. These issues, however, will be addressed separately.

This paper is organized as follows. Section II summarizes the exact memory function expressions for the partial intermediate scattering functions of a colloidal mixture, on which we base our theory. In Secs. III and IV we explain the approximations that render these exact results into an approximate closed self-consistent system of equations for these dynamic properties. The quantitative application of the theory to a simple model system is contained in Sec. V, and the main conclusions are summarized in Sec. VI.

## II. EXACT RESULTS

Although a colloidal dispersion 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 degrees of freedom of the  $N$  colloidal particles, i.e., the many-body Langevin equation [27–29]. It is generally accepted that this system of  $N$  stochastic equations for the velocities of the  $N$  colloidal particles, coupled together through the direct and hydrodynamic interaction forces between the particles, constitutes an adequate microscopic description of the dynamics of the suspension [4,5]. The aim of the statistical mechanical theory of colloid dynamics then consists of the derivation of a time-evolution equation for the *macroscopic* variables of the system, starting from the *microscopic* description provided by the  $N$ -particle Langevin equation, or other representation of the microscopic dynamics [6,7].

Let us consider a colloidal system formed by  $N$  suspended particles with positions  $\mathbf{r}_i(t)$  and velocities  $\mathbf{v}_i(t)$  at time  $t$  ( $i = 1, 2, \dots, N$ ). Let us assume that these  $N$  particles belong to  $\nu$  species (labeled  $\alpha = 1, 2, \dots, \nu$ ), with  $N_\alpha$  of them pertaining to species  $\alpha$ , such that their number concentration is  $n_\alpha \equiv N_\alpha/V$ , where  $V$  is the volume, and with  $N_1 + N_2 + \dots + N_\nu = N$ . The microscopic expression for the macroscopic variable representing the local concentration of particles of species  $\alpha$  at position  $\mathbf{r}$  and time  $t$  is given by

$$n_\alpha(\mathbf{r}, t) = \sum_{i=1}^{N_\alpha} \delta(\mathbf{r} - \mathbf{r}_i^{(\alpha)}(t)). \quad (1)$$

All the relevant information on the macroscopic dynamic behavior of an equilibrium multicomponent colloidal suspension is contained in the partial *van Hove functions* [30],  $G_{\alpha\beta}(r, t)$ . These are the time-dependent correlation functions of the fluctuations  $\delta n_\alpha(\mathbf{r}, t)$  of the instantaneous local concentration of colloidal particles of species  $\alpha$ ,  $n_\alpha(\mathbf{r}, t)$ , at position  $\mathbf{r}$  and time  $t$ , around its bulk equilibrium value,  $n_\alpha$ , i.e.,

$$G_{\alpha\beta}(|\mathbf{r} - \mathbf{r}'|, t) \equiv \frac{1}{\sqrt{n_\alpha n_\beta}} \langle \delta n_\alpha(\mathbf{r}, t) \delta n_\beta(\mathbf{r}', 0) \rangle, \quad (2)$$

with  $\delta n_\alpha(\mathbf{r}, t) \equiv n_\alpha(\mathbf{r}, t) - n_\alpha$ . Experimental techniques allow the determination of these functions, or of linear combinations of their spatial Fourier transforms  $F_{\alpha\beta}(k, t)$ ,

$$F_{\alpha\beta}(k, t) = \int d\mathbf{r} G_{\alpha\beta}(r, t) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (3)$$

referred to as the *partial intermediate scattering functions*. These functions can also be written as the time-dependent correlation function of the macroscopic variable  $\delta n_\alpha(\mathbf{k}, t)$ ,

$$F_{\alpha\beta}(k, t) = \langle \delta n_\alpha(\mathbf{k}, t) \delta n_\beta(-\mathbf{k}, 0) \rangle, \quad (4)$$

where  $\delta n_\alpha(\mathbf{k}, t)$  is defined as

$$\delta n_\alpha(\mathbf{k}, t) = \frac{1}{\sqrt{N_\alpha}} \sum_{i=1}^{N_\alpha} e^{i\mathbf{k}\cdot\mathbf{r}_i^{(\alpha)}(t)}. \quad (5)$$

Except for the normalization factor  $(N_\alpha)^{-1/2}$ , this is essentially the Fourier transform of the local concentration  $n_\alpha(\mathbf{r}, t)$  in Eq. (1) above.

From the last two equations, one can see that  $F_{\alpha\beta}(k, t)$  can be written as the sum of its ‘‘self’’ and ‘‘distinct’’ parts,

$$F_{\alpha\beta}(k, t) = F_{\alpha\beta}^s(k, t) + F_{\alpha\beta}^d(k, t), \quad (6)$$

where

$$F_{\alpha\beta}^s(k, t) = \delta_{\alpha\beta} \frac{1}{N_\alpha} \left\langle \sum_{i=1}^{N_\alpha} e^{i\mathbf{k} \cdot [\mathbf{r}_i^{(\alpha)}(t) - \mathbf{r}_i^{(\alpha)}(0)]} \right\rangle \equiv \delta_{\alpha\beta} F_{\alpha\beta}^s(k, t), \quad (7)$$

and

$$F_{\alpha\beta}^d(k, t) = \frac{1 - \delta_{\alpha\beta}}{\sqrt{N_\alpha N_\beta}} \left\langle \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} e^{i\mathbf{k} \cdot [\mathbf{r}_i^{(\alpha)}(t) - \mathbf{r}_j^{(\beta)}(0)]} \right\rangle + \frac{\delta_{\alpha\beta}}{N_\alpha} \left\langle \sum_{i=1}^{N_\alpha} \sum_{j \neq i}^{N_\beta} e^{i\mathbf{k} \cdot [\mathbf{r}_i^{(\alpha)}(t) - \mathbf{r}_j^{(\alpha)}(0)]} \right\rangle. \quad (8)$$

Similarly, the van Hove functions,  $G_{\alpha\beta}(r, t)$ , can also be written as the sum of their self and distinct components,

$$G_{\alpha\beta}(r, t) = G_{\alpha\beta}^s(r, t) + G_{\alpha\beta}^d(r, t), \quad (9)$$

where  $G_{\alpha\beta}^s(r, t)$  and  $G_{\alpha\beta}^d(r, t)$  are the inverse Fourier transforms of  $F_{\alpha\beta}^s(k, t)$  and  $F_{\alpha\beta}^d(k, t)$ .

Any expression for  $F_{\alpha\beta}(k, t)$  properly rooted in the  $N$ -particle Langevin equation dynamics should in principle be valid for all time regimes associated to the Brownian motion of the colloidal particles. The *diffusive* (or *overdamped*) regime corresponds to times much longer than  $\tau_B$ , the largest of the relaxation times  $\tau_B^{(\alpha)} \equiv M_\alpha / \zeta_\alpha^0$ , within which the initial velocity of any particle in the mixture is damped by frictional effects. Here,  $M_\alpha$  and  $\zeta_\alpha^0$  are, respectively, the mass and the *free-diffusion* friction coefficient (i.e., the friction coefficient in the absence of interactions with other particles) of particles of species  $\alpha$ . In the diffusive regime,  $t \gg \tau_B$ ,  $\delta n(\mathbf{r}, t)$  relaxes only through purely diffusive mechanisms. Thus one has to take the so-called overdamping limit,  $t \gg \tau_B$ , in any general time-evolution equation for  $\delta n_\alpha(\mathbf{r}, t)$  [or on the corresponding expression for  $G_{\alpha\beta}(r, t)$  or  $F_{\alpha\beta}(k, t)$ ] derived from the microscopic dynamics represented by the  $N$ -particle Langevin equations. Our present work will be based on exact results obtained in this manner [16]. The alternative approach consists of starting from an already-overdamped microscopic description, such as that provided by the  $N$ -particle Smoluchowski equation [31,32], to derive the time evolution equation for  $F_{\alpha\beta}(k, t)$  valid in the diffusive regime. As an example, we remind that Ackerson [33] approached the derivation of the time evolution equation for the intermediate scattering function,  $F(k, t)$ , for monodisperse suspensions starting from the Smoluchowski equation. Applying the projection operator formalism, he arrived at a general relaxation equation for  $F(k, t)$ . Extended to the context of mixtures, this time-evolution equation reads [10,34]

$$\frac{\partial F(k, t)}{\partial t} = -k^2 D S^{-1}(k) F(k, t) + \int_0^t M(k, t-t') S^{-1}(k) F(k, t') dt'. \quad (10)$$

In this equation,  $F(k, t)$  is a  $\nu \times \nu$  matrix (with  $\nu$  being the number of colloidal species in the mixture) whose elements are the partial intermediate scattering functions,  $F_{\alpha\beta}(k, t)$ . The elements of the matrix  $D$  are given by  $D_{\alpha\beta} \equiv \delta_{\alpha\beta} D_\alpha^0$ , with  $D_\alpha^0$  being the diffusion coefficient of species  $\alpha$  in the absence of interactions. This is related with  $\zeta_\alpha^0$  through the Einstein relation,  $D_\alpha^0 \equiv k_B T / \zeta_\alpha^0$ . The elements of the matrix  $S(k) \equiv F(k, t=0)$  are the partial static structure factors  $S_{\alpha\beta}(k)$ . These are defined in terms of the radial distribution functions [30]  $g_{\alpha\beta}(r)$  as

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + (n_\alpha n_\beta)^{1/2} h_{\alpha\beta}(k), \quad (11)$$

with  $h_{\alpha\beta}(k)$  being the Fourier transform of  $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$ .

In Eq. (10),  $M(k, t)$  is a matrix of (unknown) memory functions, which contains the effects of the direct interactions. Let us notice that Eq. (10) can also be written as an explicit expression for the Laplace transform (LT)  $F(k, z)$  of  $F(k, t)$ , in terms of the LT of the matrix  $M(k, t)$  of memory functions, as

$$F(k, z) = \{z + k^2 D S^{-1}(k) - M(k, z) S^{-1}(k)\}^{-1} S(k). \quad (12)$$

For the unknown memory matrix  $M(k, t)$  one can write expressions involving projection operators related to the Smoluchowski operator [7]. Such expressions are formal results, not very useful for practical calculations, but valuable in the determination of certain limiting conditions. In fact, those projection operator expressions served as the basis for the introduction of the mode coupling approximations developed by Nägele *et al.* [11].

Rather than using such a method, our approach employs the recently derived results of the generalized Langevin equation formalism, plus the concept of contraction of the description, applied to the context of colloidal mixtures [16]. This also leads to Eq. (12), but written as

$$F(k, z) = \{z + \{I + C(k, z)\}^{-1} k^2 D S^{-1}(k)\}^{-1} S(k). \quad (13)$$

Clearly,  $M(k, z)$  and  $C(k, z)$  must be related to each other, and the relationship is  $M(k, z) = k^2 \{I + C(k, z)\}^{-1} C(k, z) D$ . The elements of the matrix  $C(k, z)$  are referred to as the irreducible memory functions [11,35]. Thus the generalized Langevin equation approach [16] leads to the same general relaxation equation for  $F(k, z)$  in terms of the memory function  $C(k, z)$  [or  $M(k, z)$ ]. However, it also complements Eq. (13) with the following expression for the irreducible memory matrix  $C(k, z)$  in terms of a higher-order memory function  $\Delta L(k, z)$ :

$$C(k, z) = k^2 D \chi_{jj}^{-1} \{z + [L^0(k) + \Delta L(k, z)] \chi(k)^{-1}\}^{-1} \chi(k) \chi_{jj}^{-1}. \quad (14)$$

Except for the unknown memory function  $\Delta L(k, z)$ , all the other elements entering in the right-hand side (rhs) of this equation are either constants [e.g., the matrix  $D$ , defined after Eq. (10), and the diagonal matrix  $\chi_{jj}$ , defined as  $[\chi_{jj}]_{\alpha\beta} \equiv \delta_{\alpha\beta} k_B T / M_\alpha$ ] or static properties, assumed determined; the latter are defined in the Appendix and discussed in more detail in Ref. [16].

Let us also write here the corresponding results for the “self” component,  $F^s(k, z)$ , of the matrix  $F(k, z)$  [see the definition in Eq. (7)]. In this case, the results corresponding to Eqs. (13) and (14) read [16]

$$F^s(k, z) = \{z + [I + C^s(k, z)]^{-1} k^2 D\}^{-1} \quad (15)$$

and

$$C^s(k, z) = k^2 D \chi_{jj}^{s-1} \{z + [L^{0s}(k) + \Delta L^s(k, z)] \chi^s(k)^{-1}\}^{-1} \chi^s(k) \chi_{jj}^{s-1}. \quad (16)$$

Again, except for the unknown memory function  $\Delta L^s(k, z)$ , all the elements entering in the rhs of this equation are known static properties [16], summarized in the Appendix. Notice also that all the matrices involved in these equations for  $F^s(k, z)$  and  $C^s(k, z)$  are diagonal. Thus we shall denote by  $F_\alpha^s(k, z)$  and  $C_\alpha^s(k, z)$ , for example, the diagonal elements  $F^s(k, z)$  and  $C^s(k, z)$ , respectively.

Equations (13)–(16) are the main and most general results on which the present work will be based. They express the intermediate scattering functions,  $F_{\alpha\beta}(k, z)$ , and their self-diffusion part,  $F_{\alpha\beta}^s(k, z)$ , in terms of purely static properties and of the unknown memory matrices  $\Delta L(k, t)$  and  $\Delta L^s(k, t)$ . In principle, given the pair interaction potential  $u_{\alpha\beta}(r)$  between particles of species  $\alpha$  and  $\beta$ , statistical thermodynamic methods [30] allow us to calculate properties such as the radial distribution functions,  $g_{\alpha\beta}(r)$ , and the partial static structure factors,  $S_{\alpha\beta}(k)$ , needed to determine the static inputs involved in the general results in Eqs. (13)–(16). Thus the crux of the dynamic problem is the determination of the unknown memory functions  $\Delta L(k, t)$  and  $\Delta L^s(k, t)$ . Unfortunately, there is no simple first-principles approach to this problem, and hence one must resort to judicious or simple approximations. In the following section we shall present and discuss our self-consistent scheme, based on the introduction of approximations in the general results above.

At this point, however, let us consider the simplest approximation one could think of, namely, that consisting in neglecting the unknown memory functions, i.e., in writing  $\Delta L(k, z) = \Delta L^s(k, z) = 0$  in Eqs. (14) and (16). Under this approximation,  $C(k, z)$  and  $C^s(k, z)$  will read, respectively,

$$C(k, z) \approx C^{SEXP}(k, z) \equiv k^2 D \chi_{jj}^{-1} [z + L^0(k) \chi^{-1}]^{-1} \chi \chi_{jj}^{-1} \quad (17)$$

and

$$C^s \approx C^{sSEXP}(k, z) \equiv k^2 D \chi_{jj}^{s-1} [z + L^{0s}(k) \chi^{s-1}]^{-1} \chi^s \chi_{jj}^{s-1}. \quad (18)$$

This approximation, employed in Eqs. (13) and (15), leads to closed expressions for the properties  $F(k, z)$  and  $F^s(k, z)$ , which allow their calculation starting from purely static inputs. In fact, such approximation coincides with the single exponential memory (SEXP) approximation proposed by Arauz-Lara and Medina-Noyola [10]. The SEXP approximation has proved to be the simplest, yet practical, theoretical scheme to be employed in the interpretation of experimental and simulated self-diffusion results in monodisperse [7] and polydisperse [8,12,13] systems. It has also been applied to study collective-diffusion properties of monodisperse systems [14,15]. However, only until recently [16] it has been used to study collective diffusion in multicomponent systems. The SEXP approximation is exact at short times and/or large wave vectors, and will constitute a simple but non-trivial zeroth-order level approximation in the self-consistent theory that we now develop. Deviations from this approximation will be represented by nonzero values of the higher-order memory functions  $\Delta L(k, z)$  and  $\Delta L^s(k, z)$ , or deviations of the memory functions  $C(k, z)$  and  $C^s(k, z)$  from their SEXP expressions in Eqs. (17) and (18).

### III. VINEYARD-LIKE APPROXIMATIONS

The second element in the construction of our self-consistent theory is the proposal of a higher-order Vineyard-like relationship [20] between  $F(k, t)$  and  $F^s(k, t)$ . Vineyard's approximation [36] itself consists of the simplest of such relationships, namely,  $F(k, t)$  is approximated directly by  $F^s(k, t) S(k)$ . In previous work, alternative manners to refer collective dynamics to self-diffusion were studied [20]. Rather than relating  $F(k, t)$  directly to  $F^s(k, t)$ , the proposal was to approximate a memory function of  $F(k, t)$  by the corresponding memory function of  $F^s(k, t)$ .

As an illustration, consider Eqs. (13)–(16). They suggest to relate  $F(k, z)$  to  $F^s(k, z)$  through their higher-order memory functions  $\Delta L(k, z)$  and  $\Delta L^s(k, z)$ . The detailed manner in which this is done turns out to be important, as it was discussed in the context of the monodisperse case [20], in which the most accurate and fundamental proposal for a Vineyard-like connection between  $F(k, z)$  and  $F^s(k, z)$  seemed to be the following approximation:

$$\frac{\Delta L(k, z)}{L^0(k)} = \frac{\Delta L^s(k, z)}{L^{0s}(k)}. \quad (19)$$

In practice, however, we shall not use, or refer to, this approximation, since it was shown that another Vineyard-like relationship, which can be defined in terms of a simple connection between the memory functions  $C(k, z)$  and  $C^s(k, z)$ , and which does not involve explicitly the memory functions  $\Delta L(k, z)$  and  $\Delta L^s(k, z)$ , happened to be just as accurate. Such Vineyard-like approximation also preserves the exact short-time limit up to order  $t^3$  for  $F(k, t)$  and  $F^s(k, t)$ , and is defined by the general results in Eqs. (13) and (15), along with the following approximate relation [20]:

$$C(k, z)C^{SEXP}(k, z)^{-1} = C^s(k, z)C^{sSEXP}(k, z)^{-1}, \quad (20)$$

where  $C^{SEXP}(k, z)$  and  $C^{sSEXP}(k, z)$  are given, respectively, by Eqs. (17) and (18). This scheme refers both,  $F(k, z)$  and  $F^s(k, z)$ , to the knowledge of a single memory function, namely,  $C^s(k, z)$ . In what follows, we shall refer to the relationship in Eq. (20) as the *multiplicative* Vineyard-like approximation.

Let us stress that the reported study on the quantitative accuracy of several Vineyard-like approximations only referred to monodisperse systems [20]. We have also performed a few similar tests involving the model system that we shall consider later in this paper, and we found that the Vineyard-like relationship in Eq. (20) was indeed one of the most accurate. We also found, however, that an even simpler Vineyard-like relationship happened to be virtually as accurate when incorporated in the fully self-consistent scheme developed below. Such relationship reads

$$C(k, z) = C^s(k, z) + [C^{SEXP}(k, z) - C^{sSEXP}(k, z)], \quad (21)$$

which will be referred to as the *additive* Vineyard-like approximation.

Once we adopt either of these two Vineyard-like approximations [Eqs. (20) or (21)], the remaining problem is to find an additional and independent expression for  $C^s(k, z)$ . Such an expression constitutes the closure relation for the system of equations formed by the general results in Eqs. (13) and (15), complemented by either the multiplicative or the additive Vineyard-like approximations. Our proposal for such a closure relation is found in the following section.

#### IV. CLOSURE RELATION AND SELF-CONSISTENT SCHEME

The next step is, thus, finding some form of approximation for the memory function  $C^s(k, z)$ , beyond its large  $k$  limit  $C^{sSEXP}(k, z)$ . Here, too, we look for a simple physical notion that guides us, and this is the expectation that the  $k$ -dependent self-diffusion properties, represented by  $F^s(k, z)$  or  $C^s(k, z)$ , should be related in a simple manner to the ( $k$ -independent) properties that describe the Brownian motion of tagged particles. This notion is best illustrated by the well-known Gaussian approximation [4] for  $F^s_\alpha(k, t)$ , which writes

$$F^s_\alpha(k, t) = e^{-k^2 W_\alpha(t)} \quad (22)$$

where  $W_\alpha(t) = \langle [\Delta \mathbf{R}_\alpha(t)]^2 \rangle / 6$  is the mean squared displacement of a tagged particle of species  $\alpha$ . If we had an independent determination of  $W_\alpha(t)$ , then Eq. (22) provides a closed representation of self-diffusion dynamics, and, through the results of the previous section, we would also have an approximate representation of collective dynamics.

Instead of the Gaussian approximation, however, here we propose an alternative format for the approximate relationship between the  $k$ -dependent properties describing self-diffusion and the  $k$ -independent properties describing Brownian motion. For this, let us notice that in one particular limit, the function  $C^s_\alpha(k, z)$  [i.e., the diagonal, and only non-

zero, elements of  $C^s(k, z)$ ] can be identified with a well-defined property that is central to the description of the Brownian motion of tagged particles in a fluid of interacting colloidal particles. Thus one can show [5] that at long wavelengths,  $C^s_\alpha(k, z)$  converges to  $\Delta \zeta_\alpha(z) / \zeta_\alpha^0$ , i.e.,

$$\lim_{k \rightarrow 0} C^s_\alpha(k, z) = \frac{\Delta \zeta_\alpha(z)}{\zeta_\alpha^0} \equiv \Delta \zeta_\alpha^*(z), \quad (23)$$

where  $\zeta_\alpha^0$  is the free-diffusion friction coefficient of species  $\alpha$ , and  $\Delta \zeta_\alpha(z)$  is the Laplace transform of the time-dependent friction function  $\Delta \zeta_\alpha(t)$  that describes the frictional effects of the direct interactions on the Brownian motion of a tracer particle of species  $\alpha$ . This motion can be described [24] by the following generalized Langevin equation for the tracer's velocity  $\mathbf{v}_\alpha(t)$ ,

$$M_\alpha \frac{d\mathbf{v}_\alpha(t)}{dt} = -\zeta_\alpha^0 \mathbf{v}_\alpha(t) + \mathbf{f}_\alpha^0(t) - \int_0^t \Delta \zeta_\alpha(t-t') \mathbf{v}_\alpha(t') dt + \mathbf{F}_\alpha(t), \quad (24)$$

Here,  $\mathbf{f}_\alpha^0(t)$  and  $\mathbf{F}_\alpha(t)$  are the random forces, whose time-dependent correlation functions are  $\langle \mathbf{f}_\alpha^0(t) \mathbf{f}_\beta^0(0) \rangle = 6k_B T \zeta_\alpha^0 \delta_{\alpha\beta} \delta(t) \mathbf{I}$  and  $\langle \mathbf{F}_\alpha(t) \mathbf{F}_\beta(0) \rangle = 3k_B T \delta_{\alpha\beta} \Delta \zeta_\alpha(t) \mathbf{I}$ , and  $M_\alpha$  is the mass of particles of species  $\alpha$ . In a previous application of the GLE formalism to tracer diffusion [24], approximate expressions for  $\Delta \zeta_\alpha(t)$  have been derived; one of them can be written as

$$\Delta \zeta_\alpha^*(t) \equiv \frac{\Delta \zeta_\alpha(t)}{\zeta_\alpha^0} = \frac{D_\alpha^0}{3(2\pi)^3} \int d^3 \mathbf{k} k^2 F_\alpha^s(k, t) \sum_{\beta, \gamma=1}^{\nu} F_{\beta\gamma}(k, t) \times \left[ \sum_{\delta=1}^{\nu} \sqrt{\frac{n_\delta}{n_\beta}} h_{\alpha\delta} E_{\delta\beta} \right] \left[ \sum_{\eta=1}^{\nu} n_\eta h_{\alpha\eta} E_{\gamma\eta} \right], \quad (25)$$

where  $E = E(k)$  is the inverse matrix of the matrix of static structure factors,  $E(k) \equiv [S(k)]^{-1}$ , and with  $h_{\alpha\beta}(k)$  being defined in Eq. (11) above.

Thus we have two important exact limits for the memory function  $C^s_\alpha(k, z)$ , namely,

$$\lim_{k \rightarrow 0} C^s_\alpha(k, z) = \Delta \zeta_\alpha^*(z) \quad (26)$$

and

$$\lim_{k \rightarrow \infty} C^s_\alpha(k, z) = C_\alpha^{sSEXP}(k, z). \quad (27)$$

Following the attitude taken in the monocomponent version of the self-consistent theory [21], here we also propose to interpolate  $C^s_\alpha(k, z)$  between these two exact limits by means of the following expression:

$$C^s_\alpha(k, z) = C_\alpha^{sSEXP}(k, z) + [\Delta \zeta_\alpha^*(z) - C_\alpha^{sSEXP}(k, z)] \lambda_\alpha(k), \quad (28)$$

where  $\lambda_\alpha(k)$  is a phenomenological interpolating function such that  $\lambda_\alpha(k) \rightarrow 1$  for  $k \rightarrow 0$ , and  $\lambda_\alpha(k) \rightarrow 0$  for  $k \rightarrow \infty$ . In the one-component case [21], a functional form of the general type  $\lambda(k) = [1 + (k/k_c)^\nu]^{-1}$  was proposed, and the choice of the parameters  $k_c$  and  $\nu$  was made by comparing the theoretical

predictions for various values of  $k_c$  and  $\nu$  with exact (computer simulated) data for a particular model system, at a given state, and at a given time. This led to the following prescription for  $\lambda(k)$ ,

$$\lambda(k) = \frac{1}{1 + \left(\frac{k}{k_{\min}}\right)^2}, \quad (29)$$

where  $k_{\min}$  is the position of the first minimum of the static structure factor  $S(k)$  of the monodisperse system. In the multicomponent case, we found that a simple extension of this prescription, namely,

$$\lambda_\alpha(k) = \frac{1}{1 + \left(\frac{k}{k_{\min}^{(\alpha)}}\right)^2}, \quad (30)$$

with  $k_{\min}^{(\alpha)}$  being the position of the first minimum (beyond the main peak) of the partial static structure factor  $S_{\alpha\alpha}(k)$ , was also in practice the best choice.

In this manner, through Eqs. (28), (25), and (30), we have defined a closure relation for the unknown memory functions  $C_\alpha^s(k, z)$ , which is thus expressed in terms of the diffusion coefficients  $D_\alpha^0$  and of the purely static properties involved in the integrand of Eq. (25) and in  $C_\alpha^{sSEXP}(k, z)$  [see Eq. (18)]. The integrand of the time-dependent friction function  $\Delta_{S_\alpha^*}^s(t)$ , Eq. (25) is also written in terms of the intermediate scattering functions  $F_{\alpha\beta}(k, t)$  and of their self components  $F_\alpha^s(k, t)$ . Thus, Eqs. (28), (25), and (30), together with the general results

$$F(k, z) = \{z + [I + C(k, z)]^{-1} k^2 D S^{-1}(k)\}^{-1} S(k) \quad (31)$$

and

$$F^s(k, z) = \{z + [I + C^s(k, z)]^{-1} k^2 D\}^{-1}, \quad (32)$$

plus either the multiplicative,

$$C(k, z) C^{SEXP}(k, z)^{-1} = C^s(k, z) C^{sSEXP}(k, z)^{-1}, \quad (33)$$

or the additive Vineyard-like relationship,

$$C(k, z) = C^s(k, z) + [C^{SEXP}(k, z) - C^{sSEXP}(k, z)], \quad (34)$$

defines our self-consistent scheme, which we shall refer to as the *self-consistent generalized Langevin equation* (SCGLE) scheme. With an illustrative purpose, in the following section, we present the results of solving numerically this system of equations for a simple model binary colloidal mixture.

## V. ILLUSTRATIVE APPLICATION

In this section we present a specific application of the self-consistent generalized Langevin equation approximate theory to illustrate its quantitative accuracy in the calculation of the self- and collective-diffusion properties of a particular model system, namely, a binary mixture of Brownian particles interacting through a hard-core pair potential of diameter  $\sigma$  (assumed the same for both species), plus a repulsive Yukawa tail of the form

$$u_{\alpha\beta}(r) = K_\alpha K_\beta \frac{e^{-\kappa\sigma(r/\sigma-1)}}{r/\sigma}. \quad (35)$$

The dimensionless parameters that define the thermodynamic state of this system are the total volume fraction  $\phi \equiv \pi/6n\sigma^3$  (with  $n$  being the total number concentration,  $n = n_1 + n_2$ ), the relative concentrations  $x_\alpha \equiv n_\alpha/n$ , and the potential parameters  $K_1$ ,  $K_2$ , and  $\kappa\sigma$ . To simplify matters, in this illustrative example we shall also assume that the free-diffusion coefficients  $D_\alpha^0$  are identical for both species, i.e.,  $D_1^0 = D_2^0 = D^0$ . Explicit values of the parameters  $\sigma$  and  $D^0$  are not needed, since the dimensionless dynamic properties, such as  $F_{\alpha\beta}(k, t)$ , only depend on the dimensionless parameters specified above, when expressed in terms of the scaled variables  $k\sigma$ , and  $t/t_0$ , where  $t_0 \equiv \sigma^2/D^0$  is the typical time it takes one particle to diffuse its own hard-sphere diameter.

Besides solving the SCGLE scheme, we also generated Brownian dynamics simulations for the static and dynamic properties of the system above. We employed a cubic simulation box with periodic boundary conditions and 1728 particles in total. Once the total number concentration is defined, the length of the simulation box is determined by  $L = (N/n)^{1/3}$ . The simulation starts from a random distribution of the particles of both species and then, using the conventional Brownian dynamics algorithm [37,38], we let the system evolve until equilibrium is reached. When the total potential energy of the system stabilizes, we proceed to the calculation of the static and dynamic properties. The time step was chosen such that the *mean squared displacement* of the particles *in one time step* was around  $10^{-2}$  times the mean interparticle distance  $d = (1/n)^{1/3}$ .

The radial distribution functions  $g_{\alpha\beta}(r)$  and the partial static structure factors  $S_{\alpha\beta}(k)$  obtained from these computer simulations served as input in the calculation of the static properties defined in the Appendix and employed in Eqs. (17), (18), and (25). In the calculation of the last term of Eqs. (40) and (44), one additional approximation was introduced: the three-particle correlation function,  $g_{\alpha\beta\gamma}^{(3)}(\mathbf{r}, \mathbf{r}')$ , was simplified using Kirkwood's superposition approximation [30],

$$g_{\alpha\beta\gamma}^{(3)}(\mathbf{r}, \mathbf{r}') = g_{\alpha\beta}(r) g_{\alpha\gamma}(r') g_{\beta\gamma}(|\mathbf{r} - \mathbf{r}'|), \quad (36)$$

plus the additional simplification of neglecting the correlations between particles  $\beta$  and  $\gamma$ , i.e., setting  $g_{\beta\gamma}(|\mathbf{r} - \mathbf{r}'|) = 1$ , in the previous equation. This simplifying approximation reduces the needed static inputs of our theory to the radial distribution functions  $g_{\alpha\beta}(r)$ . Let us also point out that completely neglecting the term involving  $g_{\alpha\beta\gamma}^{(3)}(\mathbf{r}, \mathbf{r}')$  in Eqs. (40) and (44) would introduce numerical anomalies in the results for  $C^{SEXP}(k, t)$  at certain wave vectors, of the same nature as described for monodisperse systems [15]. We found that the approximation we employed was systematically free of such an anomaly. Furthermore, in the cited reference [15], a simple estimate of the term neglected in setting  $g_{\beta\gamma}(|\mathbf{r} - \mathbf{r}'|) = 1$  was proposed. We found, however, that such an estimate is not in general useful, and hence we did not employ it here.

The self-consistent scheme consisting of the general results in Eqs. (31) and (32), together with Eqs. (28), (25), and (30), plus either the multiplicative [Eq. (33)] or the additive

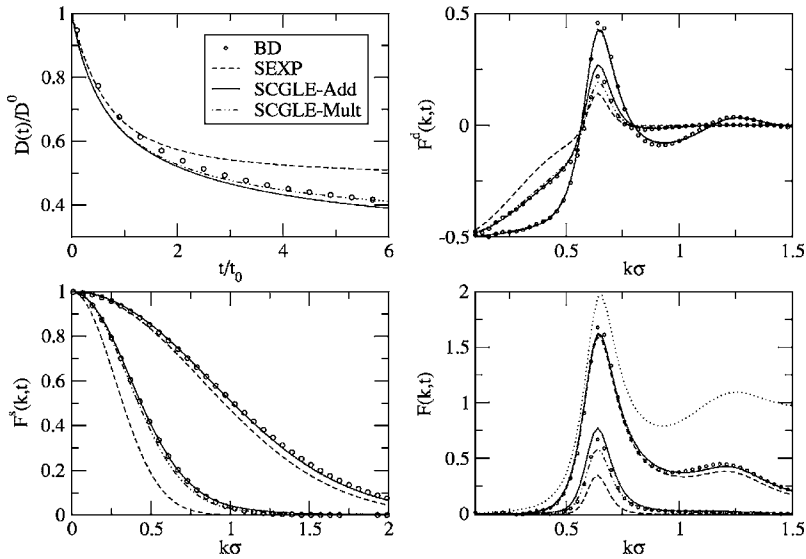


FIG. 1. Application of the SCGLE to a *monodisperse* system with  $K_1^2=K_2^2=500$  and  $\phi=0.00044$ . In the upper left panel we plot the time-dependent diffusion coefficient  $D(t)=D_1(t)=D_2(t)$ , normalized with its initial value  $D^0$ , and in the other panels we present the self, the distinct, and the total intermediate scattering functions of this monodisperse system. Symbols represent Brownian dynamics simulations data. We present the results of the SCGLE theory within the additive (solid lines) and the multiplicative (dot-dashed lines) Vineyard-like approximations. For reference, we also present the results of the SEXP approximation (dashed lines). The results for the intermediate scattering functions  $F^s(k,t)$ ,  $F^d(k,t)$ , and  $F(k,t)$  correspond to times  $t=t_0$  [upper set of curves for  $F^s(k,t)$  and  $F(k,t)$ , and more structured curves for  $F^d(k,t)$ ] and  $t=10t_0$ .

[Eq. (34)] Vineyard-like relationship, has to be solved numerically. For this, the self-consistent set of equations are written in  $t$ -space as a set of coupled integrodifferential equations. The functions of  $k$  and  $t$  are then discretized in a mesh of points large enough to ensure independence of the solution with respect to the size of the mesh. The solution of the discretized system of equations is then solved by a straightforward direct iteration method.

In this manner, we are able to determine the predictions of the SCGLE approximation for the various dynamic properties of the specific system defined above, such as the partial intermediate scattering functions,  $F_{\alpha\beta}(k,z)$ , their self-diffusion part,  $F_{\alpha\beta}^s(k,z)$ , and the time-dependent diffusion coefficient  $D_\alpha(t)$ , defined as  $D_\alpha(t) \equiv W_\alpha(t)/t$ , with  $W_\alpha(t)$  being the mean-squared displacement (msd) of particles of species  $\alpha$ . Let us first present the solution of the two versions of the SCGLE theory that result from the use of the multiplicative and the additive Vineyard-like approximations of Eqs. (33) and (34). We first consider the context of a monodisperse system, for which we take  $K \equiv K_1^2=K_2^2=500$  and  $\phi=0.00044$ . There is no special reason for choosing these spe-

cific values, or the ones to be employed later on, besides the fact that they are typical of the regime considered experimentally [8] and in previous theoretical studies of model mixtures [13,39]. In Fig. 1, the results of the SCGLE for  $D_\alpha(t)$  and for the intermediate scattering functions  $F^s(k,t)$ ,  $F^d(k,t)$ , and  $F(k,t)$  are plotted for  $t=t_0$  and  $t=10t_0$  and compared with the corresponding Brownian dynamics simulations data. As a reference, we also include the results of the SEXP approximation.

In reference to Fig. 1, let us first notice, from the decay of  $D_\alpha(t)$ , that the largest drop of this property from its initial value  $D_\alpha^0$  occurs within a time of the order of  $t_0$ , and that for  $t=10t_0$ , this property is much closer to its asymptotic value. Thus times of the order of  $t=10t_0$  are moderately long times, although the system is still relaxing. Concerning the decay of the intermediate scattering functions, at times of the order of  $t=t_0$ , the predictions of both versions of the SCGLE are indistinguishable between them and lie very close to the simulated data. Also the SEXP approximation is a good approximation, although for the *self* intermediate scattering function it relaxes a bit faster. For the longer time  $t=10t_0$ , we see that

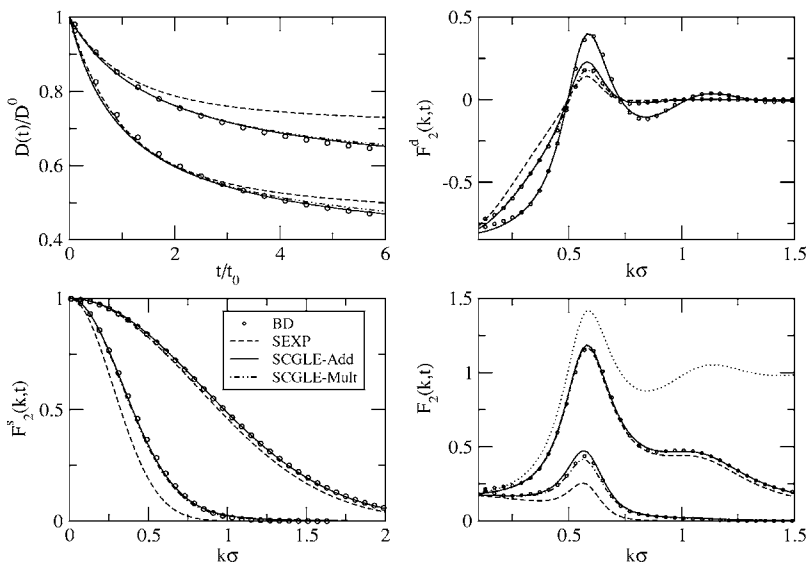


FIG. 2. Application of the SCGLE to a bidisperse system with  $K_1=10$ ,  $K_2=10\sqrt{5}$ ,  $\phi_1=0.00022$ , and  $\phi_2=0.00022$ . In the upper left panel we plot the time-dependent diffusion coefficients  $D_1(t)$  and  $D_2(t)$ , normalized with their initial values  $D_\alpha^0$  (the upper curves corresponding to species 1). In the other panels we present the self, the distinct, and the total intermediate scattering functions of the more interacting species (species 2), for the same times as in Fig. 1. The symbology and conventions are the same as in Fig. 1. For reference, the static structure factor of species 2 (dotted line) is also shown.

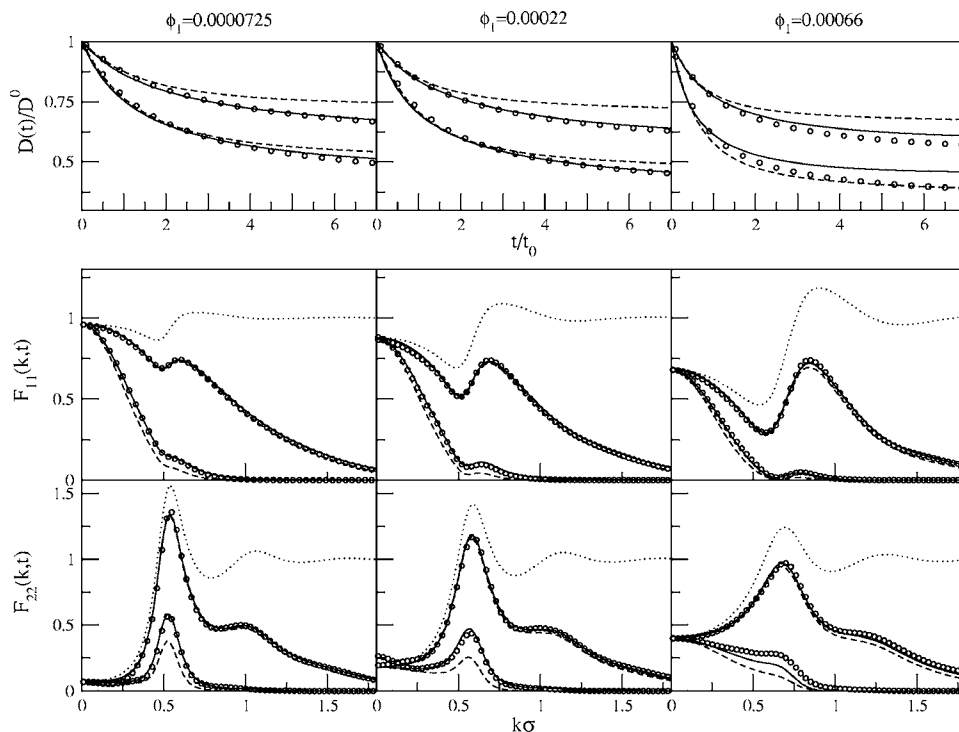


FIG. 3. Application of the SCGLE, within the additive Vineyard-like approximation, to bidisperse systems with  $K_1=10$ ,  $K_2=10\sqrt{5}$ . The volume fraction of the more interacting species is kept fixed at  $\phi_2=0.00022$  and  $\phi_1$  takes the values  $\phi_1=0.0000725$  (left column),  $0.00022$  (center column), and  $0.00066$  (right column), corresponding to  $x_1=0.25$ ,  $x_1=0.5$ , and  $x_1=0.75$ . In the upper row, the time-dependent diffusion coefficients are plotted for both species (upper curve corresponding to species 1), whereas the intermediate scattering functions for both species are plotted in the lower rows for  $t=t_0$  and  $t=10t_0$ . The symbology and conventions are the same as in Fig. 1. For reference, the partial static structure factors (dotted lines) are also included.

the SEXP exhibits large departures from the simulated data. Also the two versions of the SCGLE cease to coincide, although the corresponding results seem to bracket the simulation data, with the multiplicative version relaxing a little bit faster. This type of comparison was made for other systems, with similar conclusions, as illustrated in Fig. 2, where we present a similar comparison for a mixture with  $K_1=10$  and  $K_2=10(5)^{1/2}$ . This mixture corresponds to the system in Fig. 1 in which half of the particles were replaced by particles of a less interacting species (species 1). As we can see from the results in this figure, the qualitative scenario is quite similar to that in Fig. 1. Notice that in this case we only display the dynamics of the more interacting species; however, the qualitative trends are also observed in the dynamics of species 1.

In Fig. 3 we illustrate the full intermediate scattering function of both species in the mixture above (central column). In this figure we also present results for the same mixture in which we vary the concentration of the least interacting species (species 1) keeping fixed the concentration of particles of species 2 at the same value as in Fig. 2. Thus the column at the left corresponds to the same system as in Fig. 2, to which we subtract particles of species 1 to adjust to a molar fraction  $x_1=0.25$  (Fig. 2, and the central column of Fig. 3 corresponds to  $x_1=0.5$ ). We notice that for this case, the agreement of the SCGLE results with the simulation data is of the same quality as in the cases illustrated in Figs. 1 and 2. In contrast, in the right column of Fig. 3, we illustrate one regime in which the performance of the SCGLE is not impressive at the longest times for the dynamics of the more interacting species. This corresponds to the mixture in Fig. 2, to which we add particles of species 1 to adjust to a molar fraction  $x_1=0.75$ , keeping fixed the concentration of particles of species 2. In this case, the dynamics of the more abundant but least interacting species is well-described by the SCGLE approximation, but the accuracy of the results for the dynam-

ics of the more interacting species deteriorates somewhat at long times. This is also observed in the comparison of the SCGLE prediction for the time-dependent diffusion coefficient with the corresponding simulation data of this species (lower curves of the upper right panel of Fig. 3). This relative failure of the SCGLE approximation to predict accurately enough the long-time dynamics of the more interacting species is probably due to the high concentration of species 1. At this point, however, our intention is only to illustrate the predictive capability of the SCGLE scheme, including the regimes in which this scheme may encounter limitations. Overall, however, the results presented in these figures demonstrate that this theoretical scheme can be applied to specific model systems with a high level of qualitative and quantitative accuracy.

## VI. CONCLUSIONS

In this paper we have introduced a self-consistent theory for the dynamics of colloidal mixtures in the absence of hydrodynamic interactions. This was based on the recently derived [16] general and exact results for the self and collective intermediate scattering functions of the mixture in terms of a hierarchy of memory functions [Eqs. (31) and (32)], complemented with a number of approximations. The most significant of such approximations was the Vineyard-like approximation between collective and tracer diffusion, which allows us to write the dynamics in terms of a single memory function, namely, that related to tracer diffusion. In this paper we considered two alternative versions of this approximation, which we referred to as the multiplicative [Eq. (33)] and the additive [Eq. (34)] Vineyard-like approximations. The second approximation consists of the interpolation of this only unknown memory function between its two exact limits at small and large wave vectors, by means of a phenomenologi-



cal Lorentzian interpolating function with its inflection point located at the position of the first minimum of the partial static structure factors.

In reference to the relatively arbitrary choice of this particular functional form for  $\lambda(k)$ , and of the specific Vineyard-like approximation, we may say that this corresponds to the arbitrariness of the choice of a particular vertex function in the self-consistent theories derived within the well-known mode coupling approaches [5,7,11,17,18]. Also in these theories, a sensible guess of the right vertex function must compensate our otherwise fundamental ignorance of the detailed manner in which the many-body microscopic dynamics determines the macroscopic laws that describe the experimentally observed behavior of our system.

The small wave-vector exact limit of the interpolated self memory function involves a time-dependent friction function, for which we took a well-established general approximate result [24], previously derived within the generalized Langevin equation formalism. This general result expresses the time-dependent friction function in terms of the partial intermediate scattering functions, thus closing the system of equations into a fully self-consistent scheme. This extends to mixtures a recently proposed self-consistent theory developed for monodisperse suspensions [21,22], whose predictions turned out to be highly accurate in their quantitative application to a set of specific model systems including short- and long-ranged pairwise forces in two and three dimensions. As we have demonstrated now, the level of accuracy of the present extension seems to be equally precise, at least when applied to the representative model of a binary dispersion in the absence of hydrodynamic interactions.

In the specific application of the SCGLE scheme we also compared the two versions of the Vineyard-like approximation. In the previous application to monodisperse suspensions [22], only the multiplicative version [Eq. (33)] was employed. In the present application of the extension to mixtures, we also solved the SCGLE scheme within the additive version [Eq. (34)]. The main conclusion of these comparisons in Figs. 1 and 2 above is that the numerical inconsistencies observed between the SCGLE within the multiplicative and the additive Vineyard-like approximation are not sufficient to discriminate between them concerning the possible systematic superiority of either of them. Both reproduce the dynamics of the mixture with similar levels of accuracy. In many circumstances, the results of these two versions bracket the simulation results, with the multiplicative version relaxing slightly faster.

Of course, our intention in this paper was only to present our proposal of a self-consistent scheme for the dynamics of colloidal mixtures, and to illustrate the type of applications in the context of a simple model system. In separate communications we shall describe the detailed study of the dynamics of this and other interesting model systems, as well as the application of the theory to available experimental results. One particularly interesting application of the present work refers to the specific conditions in which the spatial configuration of the particles of one species is quenched, thus simulating a matrix of fixed obstacles or a porous medium. The experimental realization of these conditions can be reached in at least one manner, namely, in quasi-two-dimensional dis-

persions confined between two glass plates [40]. The theoretical analysis of such experiments constitutes a particular application of the present theory, as we shall report elsewhere [41].

## ACKNOWLEDGMENTS

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## APPENDIX

In this Appendix we summarize the expressions for the static properties entering in Eqs. (13)–(16), and assumed determination by statistical thermodynamic methods. Thus  $\chi(k)$  is given by

$$\chi(k) = (k_B T)^2 M^{-1} [\mathcal{I}(k) + I - S^{-1}(k)] M^{-1}, \quad (\text{A1})$$

where  $I$  is the  $\nu \times \nu$  identity matrix,  $S(k)$  is the matrix of static structure factors, and  $M$  is the matrix with elements  $M_{\alpha\beta} \equiv M_\alpha \delta_{\alpha\beta}$ , where  $M_\alpha$  is the mass of particles of species  $\alpha$ . The elements of the matrix  $\mathcal{I}(k)$  are defined as

$$\begin{aligned} \mathcal{I}_{\alpha\beta}(k) = & \delta_{\alpha\beta} \frac{1}{k^2} \int d^3\mathbf{r} \sum_{\gamma=1}^{\nu} n_\gamma g_{\alpha\gamma}(r) \frac{\partial^2}{\partial z^2} \beta u_{\alpha\gamma}(r) \\ & - \sqrt{n_\alpha n_\beta} \frac{1}{k^2} \int d^3\mathbf{r} \alpha_\beta g_{\alpha\beta}(r) \cos(kz) \frac{\partial^2}{\partial z^2} \beta u_{\alpha\beta} \end{aligned} \quad (\text{A2})$$

whereas  $L^0(k)$  is given by [16]

$$\begin{aligned} L^0(k) = & -k^{-4} D^{-1} m^{(3)} D^{-1} - k^2 [\chi D \chi + \chi D S^{-1} + S^{-1} D \chi \\ & + S^{-1} D S^{-1}], \end{aligned} \quad (\text{A3})$$

with  $m^{(3)}(k)$  being the matrix of third moments of  $F(k, t)$ , with elements given by [10]

$$\begin{aligned}
m_{\alpha\beta}^{(3)}(k) = & -k^6 D_\alpha^{\circ 3} \delta_{\alpha\beta} - 3\delta_{\alpha\beta} k^2 D_\alpha^{\circ 3} \int d\mathbf{r} \sum_{\gamma=1}^2 n_\gamma g_{\alpha\gamma}(r) (\mathbf{k} \cdot \nabla)^2 \beta u_{\alpha\gamma}(r) - \delta_{\alpha\beta} D_\alpha^{\circ 2} \int d\mathbf{r} \sum_{\gamma=1}^2 (D_\alpha^\circ + D_\gamma^\circ) n_\gamma g_{\alpha\gamma}(r) [(\mathbf{k} \cdot \nabla) \nabla \beta u_{\alpha\gamma}(r)]^2 \\
& - \delta_{\alpha\beta} D_\alpha^{\circ 3} \int d\mathbf{r} d\mathbf{r}' \sum_{\gamma,\lambda=1}^2 n_\gamma n_\lambda g_{\alpha\gamma\lambda}(r, r') (\mathbf{k} \cdot \nabla) (\mathbf{k} \cdot \nabla') (\nabla \cdot \nabla') \beta u_{\alpha\gamma}(r) \beta u_{\alpha\lambda}(r') + D_\alpha^\circ D_\beta^\circ \sqrt{n_\alpha n_\beta} \int d\mathbf{r} (D_\alpha^\circ + D_\beta^\circ) g_{\alpha\beta}(r) \\
& \times [\cos(\mathbf{k} \cdot \mathbf{r}) [(\mathbf{k} \cdot \nabla) \nabla \beta u_{\alpha\beta}(r)]^2 - \sin(\mathbf{k} \cdot \mathbf{r}) (\mathbf{k} \cdot \nabla)^3 \beta u_{\alpha\beta}(r)] + D_\alpha^\circ D_\beta^\circ \sqrt{n_\alpha n_\beta} \int d\mathbf{r} d\mathbf{r}' \cos(\mathbf{k} \cdot \mathbf{r}) \\
& \times \sum_{\gamma=1}^2 D_\alpha^\circ n_\gamma g_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}') (\mathbf{k} \cdot \nabla) (\mathbf{k} \cdot \nabla') (\nabla \cdot \nabla') \beta u_{\alpha\beta}(r) \beta u_{\alpha\gamma}(r') \\
& + D_\alpha^\circ D_\beta^\circ \sqrt{n_\alpha n_\beta} \int_{sym} - D_\alpha^\circ D_\beta^\circ \sqrt{n_\alpha n_\beta} \int d\mathbf{r} d\mathbf{r}' \cos(\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')) \\
& \times \sum_{\gamma=1}^2 D_\gamma^\circ n_\gamma g_{\alpha\beta}^{(3)}(\mathbf{r}, \mathbf{r}') (\mathbf{k} \cdot \nabla) (\mathbf{k} \cdot \nabla') (\nabla \cdot \nabla') \beta u_{\alpha\gamma}(r) \beta u_{\beta\gamma}(r'). \tag{A4}
\end{aligned}$$

In this equation,  $g_{\alpha\beta}(r)$  and  $u_{\alpha\beta}(r)$  are, respectively, the radial distribution function and the pair potential between particles of species  $\alpha$  and  $\beta$ ;  $g_{\alpha\beta\gamma}^{(3)}(\mathbf{r}, \mathbf{r}')$  is the three-particle correlation function. Finally, the integral denoted by  $\int_{sym}$  is obtained from the integral in its preceding term upon the interchange of the indices  $\alpha$  and  $\beta$ .

The corresponding results for the “self” component are, respectively,

$$\chi^s(k) = (k_B T)^2 M^{-2} \mathcal{T}^s(k), \tag{A5}$$

where

$$\mathcal{T}_{\alpha\beta}^s(k) = \delta_{\alpha\beta} \frac{1}{k^2} \int d^3\mathbf{r} \sum_{\gamma=1}^v n_\gamma g_{\alpha\gamma}(r) \frac{\partial^2}{\partial z^2} \beta u_{\alpha\gamma}(r) \tag{A6}$$

and

$$L^{0s} = -k^4 D^{-1} m^{s(3)} D^{-1} - k^2 D(\chi^s + I)^2 \tag{A7}$$

with the elements of  $m^{s(3)}(k)$  given by [10]

$$\begin{aligned}
m_{\alpha\beta}^{s(3)}(k) = & -k^6 D_\alpha^{\circ 3} \delta_{\alpha\beta} - 3\delta_{\alpha\beta} k^2 D_\alpha^{\circ 3} \int d\mathbf{r} \sum_{\gamma=1}^2 n_\gamma g_{\alpha\gamma}(r) \\
& \times (\mathbf{k} \cdot \nabla)^2 \beta u_{\alpha\gamma}(r) - \delta_{\alpha\beta} D_\alpha^{\circ 2} \int d\mathbf{r} \\
& \times \sum_{\gamma=1}^2 (D_\alpha^\circ + D_\gamma^\circ) n_\gamma g_{\alpha\gamma}(r) [(\mathbf{k} \cdot \nabla) \nabla \beta u_{\alpha\gamma}(r)]^2 \\
& - \delta_{\alpha\beta} D_\alpha^{\circ 3} \int d\mathbf{r} d\mathbf{r}' \sum_{\gamma,\lambda=1}^2 n_\gamma n_\lambda g_{\alpha\gamma\lambda}^{(3)}(r, r') (\mathbf{k} \cdot \nabla) \\
& \times (\mathbf{k} \cdot \nabla') (\nabla \cdot \nabla') \beta u_{\alpha\gamma}(r) \beta u_{\alpha\lambda}(r'). \tag{A8}
\end{aligned}$$

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- [1] A. Imhof and J. K. G. Dhont, Phys. Rev. Lett. **75**, 1662 (1995).  
[2] A. Imhof and J. K. G. Dhont, Phys. Rev. E **52**, 6344 (1995).  
[3] N. J. Wagner and A. T. J. M. Woutersen, J. Fluid Mech. **278**, 267 (1994).  
[4] P. N. Pusey, in *Liquids, Freezing and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, Amsterdam, 1991), Chap. 10.  
[5] W. Hess and R. Klein, Adv. Phys. **32**, 173 (1983).  
[6] J. K. G. Dhont, *An Introduction to Dynamics of Colloids* (Elsevier, Amsterdam, 1996).  
[7] G. Nägele, Phys. Rep. **272**, 215 (1996).  
[8] R. Krause *et al.*, Physica A **178**, 241 (1991).  
[9] T. Ohtsuki, Physica A **110**, 606 (1982).  
[10] J. L. Arauz-Lara and M. Medina-Noyola, Physica A **122**, 547 (1983).  
[11] G. Nägele, J. Bergenholtz, and J. K. G. Dhont, J. Chem. Phys. **110**, 7037 (1999).  
[12] M. Chavez-Páez, J. L. Arauz-Lara, and M. Medina-Noyola, J. Mol. Liq. **71**, 245 (1997).  
[13] J. L. Arauz-Lara *et al.*, Prog. Colloid Polym. Sci. **84**, 377 (1991).  
[14] J. A. López-Esquivel and J. L. Arauz-Lara, J. Chem. Phys. **96**, 1651 (1992).  
[15] H. Acuña-Campa and M. Medina-Noyola, J. Chem. Phys. **113**, 869 (2000).  
[16] M. A. Chávez-Rojo and M. Medina-Noyola (unpublished).  
[17] G. Nägele and J. K. G. Dhont, J. Chem. Phys. **108**, 9566 (1998).  
[18] G. Nägele and J. Bergenholtz, J. Chem. Phys. **108**, 9893 (1998).

- (1998).
- [19] L. Yeomans-Reyna and M. Medina-Noyola, Phys. Rev. E **62**, 3382 (2000).
- [20] L. Yeomans-Reyna, H. Acuña-Campa, and M. Medina-Noyola, Phys. Rev. E **62**, 3395 (2000).
- [21] L. Yeomans-Reyna and M. Medina-Noyola, Phys. Rev. E **64**, 066114 (2001).
- [22] L. Yeomans-Reyna, H. Acuña-Campa, F. de Jesus Guevara-Rodríguez, and M. Medina-Noyola, Phys. Rev. E **67**, 021108 (2003).
- [23] M. Medina-Noyola, Faraday Discuss. Chem. Soc. **83**, 21 (1987).
- [24] M. Hernandez-Contreras, M. Medina-Noyola, and A. Vizcarra-Rendon, Physica A **234**, 271 (1996).
- [25] M. Medina-Noyola, Phys. Rev. Lett. **60**, 2705 (1988).
- [26] F. de J. Guevara-Rodríguez and M. Medina-Noyola, Phys. Rev. E **68**, 011405 (2003).
- [27] P. Langevin, Acad. Sci., Paris, C. R. **146**, 530 (1908).
- [28] P. Mazur, Physica A **110**, 128 (1982).
- [29] J. M. Deutch and I. Oppenheim, J. Chem. Phys. **54**, 3547 (1971).
- [30] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, New York, 1976).
- [31] M. V. Smoluchowski, Ann. Phys. **21**, 756 (1906).
- [32] R. Zwanzig, Adv. Chem. Phys. **15**, 325 (1969).
- [33] B. J. Ackerson, J. Chem. Phys. **69**, 684 (1978).
- [34] R. B. Jones and G. Burfield, Physica A **111**, 562 (1982).
- [35] In reality, Nägele *et al.* [11] refer to the matrix product  $[C(k, z)D]$  as the matrix of “irreducible memory functions,” a concept first introduced by B. Cichocki and W. Hess, Physica A **141**, 475 (1987).
- [36] G. H. Vineyard, Phys. Rev. **110**, 999 (1958).
- [37] D. L. Ermak and J. A. McCammon, J. Chem. Phys. **69**, 1352 (1978).
- [38] M. P. Allen and D. J. Tildesley *Computer Simulation of Liquids* (Oxford University Press, New York, 1987).
- [39] J. L. Arauz-Lara, H. Ruiz-Estrada, and M. Medina-Noyola, J. Colloid Interface Sci. **171**, 127 (1995).
- [40] G. Cruz de Leon, J. M. Saucedo-Solorio, and J. L. Arauz-Lara, Phys. Rev. Lett. **81**, 1122 (1998).
- [41] M. A. Chávez-Rojo and M. Medina-Noyola (unpublished).