Self-consistent generalized Langevin equation for colloid dynamics

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We present a general self-consistent theory of colloid dynamics which, for a system without hydrodynamic interactions, allows us to calculate $F(k,t)$, and its self-diffusion counterpart $F_S(k,t)$, given the effective interaction pair potential $u(r)$ between colloidal particles, and the corresponding equilibrium static structural properties. This theory is build upon the exact results for $F(k,t)$ and $F_S(k,t)$ in terms of a hierarchy of memory functions, derived from the application of the generalized Langevin equation formalism, plus the proposal of Vineyard-like connections between $F(k,t)$ and $F_S(k,t)$ through their respective memory functions, and a closure relation between these memory functions and the time-dependent friction function $\Delta\zeta(t)$. As an illustrative application, we present and analyze a selection of numerical results of this theory in the short- and intermediate-time regimes, as applied to a two-dimensional repulsive Yukawa Brownian fluid. For this system, we find that our theory accurately describes the dynamic properties contained in $F(k,t)$ in a wide range of conditions, including strongly correlated systems, at the longest times available from our computer simulations.

I. INTRODUCTION

The description of the dynamic properties of colloidal suspensions is an important experimental and theoretical problem of current interest. Over the years, the development of a fully satisfactory microscopic description of colloid dynamics has proved to be a challenging task [1,2]. One would like to see a general and systematic theory, firmly grounded on well-established fundamental principles, involving only a few physically transparent assumptions and approximations, and requiring, as the only input, well-defined microscopic parameters. From a more practical perspective, one would also expect such a theory to be simple enough to allow the nonspecialist to perform extensive applications to the interpretation of experimental measurements in a variety of systems and conditions. Of course, all these boundary conditions are virtually impossible to meet by a single grand theoretical formalism. As a result, what we have is a rather diverse array of approaches, formal derivations, exact and approximate results for various limiting conditions and cases, and a few effective or physically intuitive shortcuts to the most difficult aspects of this complex many-body problem [3–15]. Taken together, all these theoretical developments, mostly produced within the last 20 years, have provided a partial but sound theoretical interpretation of a large number of experimental facts. These involve important effects present in everyday colloidal suspensions, such as, charge effects in electrostatically stabilized suspensions and the effects of direct and hydrodynamic interactions in hard-sphere-like suspensions. We must say, however, that most of the quantitative tests of the theory have been related, so far, to the description of *self-* or *tracer*-diffusion phenomena, in which one measures averaged properties of the Brownian motion of individual particles. In contrast, in *collective*-diffusion experiments one measures the relaxation of the local concentration fluctuations [1]. These are governed by some form of generalized diffusion coefficient, although what is actually measured is the van Hove function $G(r,t)$ of the Brownian fluid, or its Fourier transform, the intermediate scattering function $F(k,t)$ [1,17,18]. This function contains, in principle, all the dynamic information of the equilibrium suspension. Thus, the development of conceptually clear, and quantitatively accurate, statistical mechanical theories is required for the fundamental understanding of this important collective-diffusion property. The present work is aimed at the development of one such theory.

Thus, in this paper we present a general self-consistent theoretical scheme that allows us to calculate $F(k,t)$ and its self-diffusion counterpart $F_S(k,t)$, given the effective interaction pair potential $u(r)$ between colloidal particles, and the corresponding equilibrium static structural properties [such as, the static structure factor $S(k)$ or the radial distribution function $g(r)$]. In the present discussion we shall have in mind a monodisperse colloidal suspension in the absence of hydrodynamic interactions, since our present aim is only to illustrate the general procedure employed to construct such a self-consistent scheme. Thus, the emphasis in this paper is on the conceptual basis of the approximations introduced in our theory, rather than on the details of its application to more complex systems.

Let us mention that the theory presented here is certainly not the only proposal available of a fully self-consistent scheme for the collective and self-dynamics of colloidal suspensions. In fact, as early as in 1983, Hess and Klein [4] proposed the translation to colloids of the mode-coupling self-consistent theory of molecular liquids [19,20]. Although their proposal included an initial version of a fully self-consistent scheme for colloidal systems, only until recently extensive calculations based on such theory were reported in the literature [13]. More recently, Nägele and coworkers

have developed a more elaborate version of this mode-coupling theory specifically devised to deal with colloidal liquids [14]. The resulting self-consistent scheme has been extended and applied in several interesting directions [15], although only until recently the level of its quantitative accuracy has been documented [15,16]. Our present theory shares with such proposal a number of important features, such as, the prediction of the ideal glass transition [20] in a monodisperse system, and the possibility of extension to more complex conditions. This is a consequence of the similarity in the mathematical structure of the resulting self-consistent schemes. As we shall see below, however, the main difference of our proposal, with respect to the mode-coupling approach, lies on the conceptual framework upon which our theory is ζ built.

Our theory is explicitly based on the formalization of two physically intuitive notions, namely, that collective diffusion should be related in a simple manner to self-diffusion, and that space-dependent self-diffusion, in its turn, should be related in a simple manner to the mean squared displacement (or other k-independent self-diffusion property). The development of our theory will involve four distinct fundamental steps. The first of them consists of the derivation of the most general and exact expressions for $F(k,z)$ and $F_S(k,z)$ in terms of a hierarchy of memory functions. The general method (i.e., the generalized Langevin equation approach [7,21]) employed to derive such exact expressions, along with the most general results, has been explained and illustrated in a recent work [22]. The second step consists of the formalization of the notion that collective dynamics should somehow be simply related to self-dynamics. Vineyard's approximation [23] is a simple (although qualitatively and quantitatively rather primitive [17,18]) implementation of this idea. This aspect has also been discussed separately; thus, in Ref. [24] the general expressions for $F(k,z)$ and $F_S(k,z)$ in terms of higher-order memory functions have been employed to propose and test a hierarchy of Vineyard-like approximations. Adopting any of these approximations, reduces the problem of colloid dynamics to the determination of $F_S(k,z)$ or any of its memory functions. The third basic step of the present theory consists of the proposal for the determination of $F_S(k,t)$. This step will be based on the physically intuitive expectation that space-dependent self-diffusion [represented by $F_S(k,t)$] should be simply related to the properties that characterize the Brownian motion of individual particles [1,4], just like in the Gaussian approximation, which expresses $F_S(k,t)$ in terms of the mean-squared displacement $W(t)$ as $F_S(k,t) = e^{-k^2 W(t)}$. In the present paper we propose an analogous connection, but at the level of the memory functions of $F_S(k,t)$ and $W(t)$. The memory function of $W(t)$ is the so-called time-dependent friction function $\Delta\zeta(t)$. As a final step in the development of our theory, we shall rely on the results of the generalized Langevin equation formalism for tracer diffusion [7], which leads to an expression for $\Delta\zeta(t)$ in terms of $F(k,t)$ and $F_S(k,t)$. Such closure relation finally determines our fully self-consistent theory of colloid dynamics.

In the following section we summarize the main results of Refs. [22] and [24], which contain the elements involved in the first two steps referred to above. These are, respectively, the general memory-function expressions for $F(k,t)$ and $F_S(k,t)$, and the Vineyard-like relationships between these two properties. In Sec. III we describe the remaining steps of the development of our theory, which finally lead to our fully self-consistent scheme. In Sec. IV we present and analyze a selection of illustrative results of the numerical solution of this theory in the short and intermediate times, as applied to a specific model system, namely, a two-dimensional repulsive Yukawa Brownian fluid. For this system we also perform Brownian dynamics computer simulations, with the idea of calibrating the qualitative and quantitative accuracy of this theory in the time regimes referred to above. Section V summarizes the main conclusions of this work, and discusses the potential applications of the theory developed here.

II. GENERAL RESULTS AND VINEYARD-LIKE APPROXIMATIONS

The intermediate scattering function $F(k,t)$ of a colloidal fluid contains the most relevant information on the dynamic properties of such systems [1]. This function is the spatial Fourier transform of the van Hove function $G(r,t)$ that measures the spatial and temporal correlations of the fluctuations $\delta n(\mathbf{r},t) \equiv n(\mathbf{r},t) - n$ of the local concentration $n(\mathbf{r},t)$ at position $\mathbf{r}$ and time t around its equilibrium bulk average n, i.e., $G(|\mathbf{r}-\mathbf{r}'|;t) \equiv \langle \delta n(\mathbf{r},t) \delta n(\mathbf{r}',0) \rangle$, where the angular brackets indicate average over the equilibrium ensemble [3,4]. A closely related property is the so-called *self-intermediate* scattering function $F_S(k,t)$. This is defined as $F_S(k,t) \equiv \langle e^{i\mathbf{k}\cdot\Delta\mathbf{R}(t)} \rangle$, where $\Delta\mathbf{R}(t)$ is the displacement at time t of any of the particles of the Brownian fluid.

In previous related work [22,25], the generalized Langevin equation (GLE) approach, and the concept of the contraction of the description [7,21], was employed to derive the most general time-evolution equation for the fluctuations $\delta n(\mathbf{r},t)$ of a monodisperse colloidal suspension in the absence of hydrodynamic interactions. In such derivation, the assumed underlying microscopic N-particle dynamics was provided by the many-particle Langevin equation [1]. As a result, expressions are derived for $F(k,t)$ [or its Laplace transform $F(k,z)$] in terms of a hierarchy of memory functions, and of static structural properties of the Brownian fluid [22]. In these expressions, the Brownian relaxation time $\tau_B \equiv M/\zeta^0$ (or the corresponding frecuency $z_B \equiv \tau_B^{-1}$) appears, where M and ζ^0 are, respectively, the mass and the solvent-friction coefficient of each particle in the suspension. In the absence of friction ($\zeta^0 \to 0$), these expressions correspond to those of a simple atomic liquid [18]. In the presence of friction, and in order to ''tune'' these expressions to the time regime normally probed by dynamic light scattering experiments, or by Brownian dynamics simulations, the limit $t \gg \tau_B$, or $z \ll z_B$, must be taken. Taking this, so-called ''overdamping'' limit [4], requires a careful analysis, which was the main subject of Ref. [22]. As a result, one gets the most general expression for $F(k,t)$ that describes the dynamics of the suspension in the diffusive regime (i.e., for times $t \gg \tau_B$). The resulting ''overdamped'' expressions for $F(k,z)$,

along with the corresponding result for $F_S(k,z)$, constitute the starting point of the present discussion.

According to Ref. [22], the most general expression for $F(k,z)$ in the diffusive regime can be written as

$$F(k,z) = \frac{S(k)}{z + \dfrac{k^2 D_0 S^{-1}(k)}{1 + C(k,z)}} \qquad (2.1)$$

with the memory function $C(k,z)$ given by

$$C(k,z) = \frac{k^2 D_0 \chi(k)}{z + \chi^{-1}(k) L^0(k) + \chi^{-1}(k) \Delta L(k,z)}, \qquad (2.2)$$

where $D_0 = k_B T/\zeta^0$ is the free-diffusion coefficient of each particle ($k_B T$ being the thermal energy), $S(k)$ the static structure factor, and $\chi(k)$ the static correlation function of the fluctuations of the configurational component of the stress tensor of the Brownian fluid (Notice that in Ref. [22], $\chi(k)$ and $\Delta L(k,z)$ carry a subindex ''UU,'' which we shall drop systematically in this paper). $\chi(k)$ and $L^0(k)$ are static properties that can be written [see Eqs. (A6) and (A7) of the Appendix, respectively] in terms of the two- and three-particle correlation functions $g(r)$ and $g^{(3)}(\mathbf{r},\mathbf{r}')$, which are assumed to be known. Thus, the only unknown in the expression for $F(k,z)$ in Eqs. (2.1) and (2.2) is the memory function $\Delta L(k,z)$.

The corresponding results for $F_S(k,z)$ can be written as

$$F_S(k,z) = \frac{1}{z + \dfrac{k^2 D_0}{1 + C_S(k,z)}}, \qquad (2.3)$$

where

$$C_S(k,z) = \frac{k^2 D_0 \chi_S(k)}{z + \chi_S^{-1}(k) L_S^0(k) + \chi_S^{-1} \Delta L_S(k,z)} \qquad (2.4)$$

with $\chi_S(k)$ and $L_S^0(k)$ also defined in the Appendix [Eqs. (A8) and (A9), respectively].

Let us notice that the general expressions in Eqs. (2.1) and (2.3) for $F(k,z)$ and $F_S(k,z)$ in terms of the memory functions $C(k,z)$ and $C_S(k,z)$ can also be derived using alternative general theoretical frameworks. Thus, starting from the N-particle Smoluchowski dynamics, and employing projection operator techniques, Ackerson [3] derived a time-evolution equation for $F(k,z)$ and $F_S(k,z)$ which can be written as our Eqs. (2.1) and (2.3) above, provided we identify Ackerson's memory function $M(k,z)$ with $k^2 D_0 C(k,z)/[1 + C(k,z)]$, and similarly for self-diffusion. Thus, all the relevant limiting properties of $F(k,t)$ and $F_S(k,t)$ (long times, small wave vectors, etc.) discussed already by Ackerson, will be inherited by any approximate theory based on the general results in Eqs. (2.1) and (2.3). In particular, on the basis of these results we expect that $F(k,t)$ and $F_S(k,t)$ will decay exponentially at short times for all wave vectors, and at small wave vectors for all times, with decay constants $k^2 D_0 S^{-1}(k)$ and $k^2 D_0$, respectively. Also,

for all wave vectors, $F(k,t)$ and $F_S(k,t)$ are expected to decay exponentially for asymptotically long times, with decay constants $k^2 D_0 S^{-1}(k)/[1 + C(k,z=0)]$ and $k^2 D_0/[1 + C_S(k,z=0)]$, respectively (some of these general limiting behaviors are illustrated in Fig. 4 below). We should also mention that several authors, most recently Nägele and co-workers, have rederived Ackerson's results also using the projection operator formalism with the N-particle Smoluchowski dynamics. The basic general results, however, are precisely Eqs. (2.1) and (2.3) above, with $C(k,z)$ and $C_S(k,z)$ referred to as the normalized irreducible memory functions. The starting point of the approximate theory developed here are indeed these general results, but complemented with the additional information contained in Eqs. (2.2) and (2.4), which express the irreducible memory functions $C(k,z)$ and $C_S(k,z)$ in terms of the still higher-order memory functions $\Delta L(k,z)$ and $\Delta L_S(k,z)$.

The second element in the construction of our self-consistent theory is the proposal of a higher-order Vineyard-like relationship between $F(k,t)$ and $F_S(k,t)$. Vineyard's approximation consists of the simplest of such relations, namely, $F(k,t)$ is approximated directly by $F_S(k,t)S(k)$. In Ref. [24], we studied alternative, more sophisticated manners to refer collective dynamics to self-diffusion. Rather than relating $F(k,t)$ directly to $F_S(k,t)$, we proposed to approximate a memory function of $F(k,t)$ by the corresponding memory function of $F_S(k,t)$.

As an illustration, consider Eqs. (2.1)–(2.4). This suggests 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 Ref. [24]. For our present purpose, however, it is sufficient to say that the most accurate and fundamental proposal for a Vineyard-like connection between $F(k,z)$ and $F_S(k,z)$ is defined by the following approximation:

$$\frac{\Delta L(k,z)}{L^0(k)} = \frac{\Delta L_S(k,z)}{L_S^0(k)}. \qquad (2.5)$$

Taken together with Eqs. (2.1)–(2.4), this equation defines an approximate scheme that allows us to express $F(k,z)$ and $F_S(k,z)$ in terms of a single memory function, namely, $\Delta L_S(k,z)/L_S^0(k)$. As said above, this is the most accurate Vineyard-like approximation among the ones that can be suggested from the exact results for $F(k,z)$ and $F_S(k,z)$ in Eqs. (2.1)–(2.4). One reason for such accuracy is the fact that the use of the exact results in Eqs. (2.1)–(2.4) guarantees that, independently of the value of $\Delta L(k,z)$ and $\Delta L_S(k,z)$, the resulting expressions for $F(k,t)$ and $F_S(k,t)$ satisfy exactly the first three (short-time) moment conditions [5,6].

In practice, however, in this work we shall employ a Vineyard-like connection between $F(k,z)$ and $F_S(k,z)$, which is defined in terms of a simple connection between the memory function $C(k,z)$ and $C_S(k,z)$, but which happens to be just as accurate as the most sophisticated proposal in Eq. (2.5). This 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. (2.1) and (2.3), along with the following approximate relation [24]:

$$\frac{C(k,z)}{C^{SEXP}(k,z)} = \frac{C_S(k,z)}{C_S^{SEXP}(k,z)}, \qquad (2.6)$$

where $C^{SEXP}(k,z)$ and $C_S^{SEXP}(k,z)$ are given, respectively, by Eqs. (2.2) and (2.4) with $\Delta L(k,z) = \Delta L_S(k,z) = 0$ [see also Eqs. (3.8) and (3.9) below]. Just like the previous higher-order Vineyard-like approximation, this scheme refers both, $F(k,z)$ and $F_S(k,z)$, through Eqs. (2.1), (2.3), and (2.6), to the knowledge of a single memory function, namely, $C_S(k,z)$. Thus, the remaining problem is to find a closure relation for this system of equations, and our proposal for this follows in Sec. III.

III. CLOSURE RELATIONS AND SELF-CONSISTENT DYNAMICS

Conceptually, what we did in the preceding section was to write down in concrete mathematical terms the intuitive expectation that collective dynamics must be closely related to self-diffusion dynamics. As indicated at the end of last section, here we shall choose a particular proposal for such a relationship. This proposal consists of the exact results for $F(k,z)$ and $F_S(k,z)$ in terms of the memory functions $C(k,z)$ and $C_S(k,z)$ in Eqs. (2.1) and (2.3), along with the approximation for $C(k,z)$ in terms of $C_S(k,z)$ given by Eq. (2.6) above. To proceed, we need an independent closure relation between these four unknown functions, and this is the subject of this section. 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 for $F_S(k,t)$, which writes

$$F_S(k,t) = e^{-k^2 W(t)}, \qquad (3.1)$$

where $W(t) = \langle(\Delta R(t))^2\rangle/6$ is the mean-squared displacement of a tagged particle. If we had an independent determination of $W(t)$, then Eq. (3.1) provides a closed representation of self-diffusion dynamics, and, through the results of the preceding section, we would also have an approximate representation of collective dynamics.

Here, however, instead of the Gaussian approximation, we propose an alternative format for the approximate relationship between the k-dependent properties describing self-diffusion and the k-independent properties describing the Brownian motion. For this, let us notice that in one particular limit, the function $C_S(k,z)$ can be identified with a well-defined property that is central to the description of the Brownian motion of a tagged particle. Thus, one can show [4] that at long wavelengths, $C_S(k,z)$ converges to $\Delta\zeta(z)/\zeta^0$, i.e.,

$$\lim_{k\to 0} C_S(k,z) = \frac{\Delta\zeta(z)}{\zeta^0} \equiv \Delta\zeta^*(z), \qquad (3.2)$$

where ζ^0 is the friction coefficient of the tracer particle in the absence of direct interactions, and $\Delta\zeta(z)$ is the Fourier transform of the time-dependent friction function $\Delta\zeta(t)$ that describes the frictional effects of the direct interactions on the Brownian motion of a tracer particle, which can be described [7] by the following generalized Langevin equation for the tracer's velocity $\mathbf{V}(t)$:

$$M\frac{d\mathbf{V}(t)}{dt} \equiv -\zeta^o\mathbf{V}(t) + \mathbf{f}^0(t) - \int_0^t \Delta\zeta(t-t')\mathbf{V}(t')dt' + \mathbf{F}(t). \qquad (3.3)$$

Here, $\mathbf{f}^0(t)$ and $\mathbf{F}(t)$ are the random forces whose time-dependent correlation functions are $\langle\mathbf{f}^0(t)\mathbf{f}^0(0)\rangle = 6k_BT\zeta^o\delta(t)$ and $\langle\mathbf{F}(t)\mathbf{F}(0)\rangle = 3k_BT\Delta\zeta(t)$. In a previous application of the GLE formalism to tracer diffusion [7], approximate expressions for $\Delta\zeta(t)$ have been derived. One of them can be written as

$$\Delta\zeta^*(t) \equiv \frac{\Delta\zeta(t)}{\zeta^0} = \frac{k_BTn}{(2\pi)^3\zeta^0}\int d\mathbf{k}\frac{[k_z h(k)]^2}{1+nh(k)}F(k,t)F_S(k,t), \qquad (3.4)$$

where $nh(k) \equiv S(k) - 1$.

As an illustration of the type of self-consistent approximations that one can construct employing this result, along with the results of the preceding section, let us propose to approximate

$$C_S(k,z) = \Delta\zeta^*(z) \qquad (3.5)$$

not only in the limit indicated in Eq. (3.2), but for *arbitrary* wave vectors. This would then lead, using Eq. (2.3), to the following expression for $F_S(k,t)$

$$F_S(k,z) = \frac{1}{z + \dfrac{k^2 D_0}{1+\Delta\zeta^*(z)}}. \qquad (3.6)$$

If, in addition, we adopt the simplest Vineyard-like approximation, namely, $C(k,z) = C_S(k,z)$, then we have for $F(k,z)$ the following result:

$$F(k,z) = \frac{S(k)}{z + \dfrac{k^2 D_0 S^{-1}(k)}{1+\Delta\zeta^*(z)}}. \qquad (3.7)$$

Equations (3.4), (3.6), and (3.7) now constitute a closed self-consistent system of equations for $\Delta\zeta^*(z)$, $F_S(k,z)$, and $F(k,z)$. Although this is not expected to be a particularly accurate approximation, since it must fail severely in the regime of *large* wave vectors (and short times), where the approximation $C_S(k,z) = \Delta\zeta(z)$ is certainly incorrect, it serves to illustrate the procedure to construct a self-

consistent scheme for $F(k,t)$ and $F_S(k,t)$. Thus, after this illustrative exercise, let us now construct a fully self-consistent scheme that is free from the most severe of these limitations.

For this, just like in the previous illustrative exercise, we make use of the fact that $\lim_{k\to 0} C_S(k,z) = \Delta\zeta^*(z)$. However, we do not want to destroy one feature of the general results in Eqs. (2.1)–(2.4), which is equally important in the opposite limit, $k\to\infty$ (i.e., short distances, and hence, short times). We refer to the fact that these general results were written in a manner that explicitly incorporates the exact short-time behavior of $F(k,t)$ and $F_S(k,t)$ (up to order t^3), independently of the unknown memory functions $\Delta L(k,z)$ and $\Delta L_S(k,z)$. In fact, if we set $\Delta L(k,z) = \Delta L_S(k,z) = 0$ in Eqs. (2.2) and (2.4), we recover the so-called single-exponential memory (SEXP) approximation [6] for $F(k,z)$ and $F_S(k,z)$. This is about the simplest approximate theory available for self-diffusion and collective diffusion, and was originally proposed by Arauz-Lara and Medina-Noyola by imposing the explicit requirement of being exact at short times, up to order t^3. The SEXP approximation is defined by Eqs. (2.1) and (2.3), with $C(k,z)$ and $C_S(k,z)$ given by Eqs. (2.2) and (2.4) with $\Delta L(k,z) = \Delta L_S(k,z) = 0$, i.e., by

$$C^{SEXP}(k,z) = \frac{k^2 D_0 \chi(k)}{z + z_I(k)}, \tag{3.8}$$

$$C_S^{SEXP}(k,z) = \frac{k^2 D_0 \chi_S(k)}{z + z_I^{(S)}(k)}, \tag{3.9}$$

where $z_I(k) \equiv \chi^{-1}(k) L^0(k)$ and $z_I^{(S)}(k) \equiv \chi_S^{-1}(k) L_S^0(k)$. Clearly, $[z_I(k)]^{-1}$ and $[z_I^{(S)}(k)]^{-1}$ are the relaxation times of the memory functions $C^{SEXP}(k,z)$ and $C_S^{SEXP}(k,z)$, respectively.

Thus, we have two important exact limits for the memory function $C_S(k,z)$, namely,

$$\lim_{k\to 0} C_S(k,z) = \Delta\zeta^*(k) \tag{3.10}$$

and

$$\lim_{k\to\infty} C_S(k,z) = C_S^{SEXP}(k,z). \tag{3.11}$$

Our proposal of a closure relation for $C_S(k,z)$, unlike our illustrative example in Eq. (3.5), incorporates the small-k limit in Eq. (3.10) only as a limiting condition, but in the opposite limit, it incorporates the exact large wave vector condition in Eq. (3.11). Conceptually, we do this not at the level of $C_S(k,z)$, but at the level of the higher-order memory function $\Delta L_S(k,z)$ [by means of the expression in Eq. (2.4)], and require the corresponding limits at the level of $\Delta L_S(k,z)$. Thus, from Eq. (2.4), we see that the limiting behavior of $C_S(k,z)$ in Eqs. (3.10) and (3.11), translate into the following limiting conditions for $\Delta L_S(k,z)$:

$$\lim_{k\to 0} \frac{\Delta L_S(k,z)}{L_S^0(k)} = \frac{k^2 D_0 \chi_S^2(k)}{L_S^0(k)}\left[\frac{1}{\Delta\zeta^*(k)} - \frac{1}{C_S^{SEXP}(k,z)}\right], \tag{3.12}$$

and

$$\lim_{k\to\infty} \frac{\Delta L_S(k,z)}{L_S^0(k)} = 0. \tag{3.13}$$

Since, in the framework of the present work, we do not have more fundamental information from which we can derive $\Delta L_S(k,z)$, what we do is to propose judicious assumptions and guesses for this higher-order memory function. The simplest of such assumption is precisely a simple functional dependence on k that interpolates between the two limits in Eqs. (3.12) and (3.13), such as

$$\Delta L_S(k,z) = k^2 D_0 \chi_S^2(k)\left[\frac{1}{\Delta\zeta^*(k)} - \frac{1}{C_S^{SEXP}(k,z)}\right]\alpha(k), \tag{3.14}$$

where $\alpha(k)$ is a dimensionless interpolating function such that $\lim_{k\to 0}\alpha(k) = 1$, and $\lim_{k\to\infty}\alpha(k) = 0$. Equation (3.14) is finally the closure relation that we were looking for, and expresses $\Delta L_S(k,z)$ in terms of known quantities, at least once we have defined the interpolating function $\alpha(k)$. Before doing this, let us see how the closure relation in Eq. (3.14) looks like in terms of $C_S(k,z)$. For this, substitute Eq. (3.14) in Eq. (2.4), with the following result

$$C_S(k,z) = C_S^{SEXP}(k,z) + [\Delta\zeta^*(k) - C_S^{SEXP}(k,z)]\lambda(k,z), \tag{3.15}$$

with

$$\lambda(k,z) \equiv \frac{C_S^{SEXP}(k,z)\alpha(k)}{\Delta\zeta^*(k) + [C_S^{SEXP}(k,z) - \Delta\zeta^*(k)]\alpha(k)}. \tag{3.16}$$

The function $\lambda(k,z)$, for fixed z, is just another interpolating function between the two exact limits for $C_S(k,z)$ in Eqs. (3.10) and (3.11) since, from its definition in Eq. (3.16), we can see that $\lim_{k\to 0}\lambda(k,z) = 1$ and $\lim_{k\to\infty}\lambda(k,z) = 0$.

In this manner, at this point we have all the elements that we need to construct the self-consistent scheme for $F(k,t)$ and $F_S(k,t)$. This is summarized by the exact results in Eqs. (2.1)–(2.4), the Vineyard-like approximation in terms of $\Delta L(k,z)$ and $\Delta L_S(k,z)$ in Eq. (2.5), and the closure relation in Eq. (3.14), with $\Delta\zeta^*(k)$ given by Eq. (3.4). The only missing element of this scheme is the interpolating function $\alpha(k)$, for which we arbitrarily choose the following simple functional form:

$$\alpha(k) = \frac{1}{1 + \left(\dfrac{k}{k_C}\right)^\nu}. \tag{3.17}$$

The parameter k_C is the wave-vector scale, with respect to which k is small or large, and the parameter ν determines how abruptly $\alpha(k)$ goes from 1 to zero as k increases beyond k_C. For $k < k_C$ and for $k > k_C$, $C_S(k,z)$ is better approximated by the corresponding limit in Eqs. (3.10) and (3.11), respectively. One would expect that k_C must be of the order of the position of the main peak of the static structure factor $S(k)$. The fine tuning in the actual determination of the parameters k_C and ν will be done in the following section.

The scheme just explained, which involves $\Delta L(k,z)$ and $\Delta L_S(k,z)$, together with the interpolating device involving the function $\alpha(k)$, is the result of a series of basic statistical mechanical considerations and assumptions. Similar considerations could lead to several variants of this scheme, depending on which version [24] of the Vineyard-like approximation is employed, and which closure relation one adopts. The scheme just explained is indeed the most fundamental (in the sense that it involves the highest-order memory functions $L(k,z)$ and $L_S(k,z)$ considered here). We can also say

that it is quantitatively the most accurate one, according to the numerical tests that we have performed.

However, a formally simpler scheme happens to be equally accurate and fundamental, but, *a posteriori*, looks like the most obvious proposal for an ''economic'' self-consistent theory of colloid dynamics. This corresponds to employing the Vineyard-like approximation involving $C(k,z)$ and $C_S(k,z)$ in Eq. (2.6), and the closure relation for $C_S(k,z)$ in Eq. (3.15), but with an additional simplification. This consists of assuming that $\lambda(k,z)$ in this equation is not given by Eq. (3.16), but that $\lambda(k,z)$ is itself approximated by an interpolating function of the type in Eq. (3.17). This simpler self-consistent scheme can be summarized by Eqs. (2.1) and (2.3) for $F(k,z)$ and $F_S(k,z)$ in terms of $C(k,z)$ and $C_S(k,z)$, together with the Vineyard-like approximation in Eq. (2.6), and the closure relation in Eqs. (3.4) and (3.15), but with $\lambda(k,z)$ not given by Eq. (3.16), but replaced by a simple interpolating function of the type of $\alpha(k)$ in Eq. (3.17). For reference, let us summarize here the resulting self-consistent scheme for colloid dynamics that derive from the conditions just described,

$$F(k,z) = \cfrac{S(k)}{z + \cfrac{k^2 D_0 S^{-1}(k)}{1 + C^{SEXP}(k,z) + \left[\cfrac{C^{SEXP}(k,z)}{C_S^{SEXP}(k,z)} \Delta\zeta^*(z) - C^{SEXP}(k,z) \right]\lambda(k)}}, \qquad (3.18)$$

$$F_S(k,z) = \cfrac{1}{z + \cfrac{k^2 D_0}{1 + C_S^{SEXP}(k,z) + [\Delta\zeta^*(z) - C_S^{SEXP}(k,z)]\lambda(k)}}, \qquad (3.19)$$

with $\Delta\zeta^*(z)$ being the Laplace transform of

$$\Delta\zeta^*(t) = \frac{D_0 n}{(2\pi)^3} \int d\mathbf{k} \frac{[k_z h(k)]^2}{1 + nh(k)} F(k,t)F_S(k,t) \qquad (3.20)$$

and with the interpolating function $\lambda(k)$ given by

$$\lambda(k) = \frac{1}{1 + \left(\dfrac{k}{k_C}\right)^{\nu}}. \qquad (3.21)$$

In these equations, the functions $C^{SEXP}(k,z)$ and $C_S^{SEXP}(k,z)$ are given by Eqs. (3.8) and (3.9) in terms of the static properties defined in the Appendix. Thus, for a given Brownian fluid in the absence of hydrodynamic interactions, one can input in this scheme the free-diffusion coefficient D_0 along with the pair potential $u(r)$ of the direct interactions. After calculating the static properties of the Appendix by statistical thermodynamic methods, the solution of Eqs. (3.18)–(3.20) above will provide a fully self-consistent description

of the dynamic properties of the system. The only elements not yet determined with complete precision are the parameters k_C and ν of the interpolating function $\lambda(k)$. In the following section we address the problem of determining k_C and ν, by means of the actual application of this self-consistent scheme to a simple concrete model system for which Brownian dynamics simulations are available. There we also illustrate the general level of quantitative accuracy of this new theory of colloid dynamics.

IV. SPECIFIC NUMERICAL APPLICATION

In this section we present an application of the self-consistent theory just described to the calculation of the collective dynamics of a specific system, namely, a two-dimensional repulsive Yukawa Brownian fluid. For this system, we generate Brownian dynamics simulations for $F(k,t)$, with which we compare the predictions of our theory. We first compare the results of the self-consistent scheme for a fixed state, to determine the optimum choice of

the parameters ν and k_C, which, from there on, will be kept fixed. We then compare the theoretical calculations with the computer simulation data for other states of the system. Our conclusion is that the self-consistent theory exhibits a high degree of quantitative accuracy for all the states considered (including highly interacting systems), and all the regimes accessible to our computer simulations. The model system considered is defined by the pair potential

$$\beta u(r) = \begin{cases} K\dfrac{e^{-z(r/\sigma-1)}}{r/\sigma}, & r > \sigma \\ \infty, & r < \sigma \end{cases}, \qquad (4.1)$$

where σ is the hard-core diameter of the particles, K is the pair interaction energy at contact in units of $k_B T$, and z is the inverse of the screening length (in units of σ^{-1}). The basic dynamic parameter is the diffusion coefficient D_0. We shall only consider the following fixed values of the parameters K and z, namely, $K=500$ and $z=0.15$, and vary the reduced number density $n^*=n\sigma^2$, where n is the number of particles per unit area. There is no special reason for choosing this model system and these fixed values of K and z, other than the fact that this system and conditions have been studied rather extensively elsewhere [9,24,26,27]. Notice that for the values $K=500$ and $z=0.15$, the Yukawa repulsion prevents the particles from probing hard-core contact. Thus, the length scale σ does not have an important physical significance, and will only be employed as an arbitrary unit length to define dimensionless quantities such as n^*, or the dimensionless distance r/σ and dimensionless wave vector $k\sigma$. Similarly, we do not need to assign a numerical value to the free-diffusion coefficient D_0, since this parameter will be absorbed in the definition of the time scale $t_0 \equiv \sigma^2/D_0$, which will be employed to define the dimensionless time variable t/t_0. The Brownian dynamics computer simulation experiments have been described elsewhere [24,27]. Here we shall employ the computer simulation results for the radial distribution function $g(r)$, as the fundamental static structural input of our theory. This allows us to avoid at this stage one possible source of uncertainty, such as that introduced by the use of some integral equation approximation to calculate $g(r)$ from $u(r)$. From the exact (i.e., computer simulated) $g(r)$ we calculate the Fourier transform $h(k)$ of the total correlation function $h(r)=g(r)-1$, and the static structure factor $S(k)=1+nh(k)$. These quantities enter explicitly in the self-consistent scheme summarized by Eqs. (3.18)–(3.20), in which other quantities appear, namely, $C^{SEXP}(k,z)$ and $C_S^{SEXP}(k,z)$. These are written in Eqs. (3.8) and (3.9) in terms of the static properties $\chi(k)$, $\chi_S(k)$, $L^0(k)$, and $L_S^0(k)$ which, in their turn, are defined in the Appendix [Eqs. (A6), (A8), (A7), and (A9), respectively] in terms of $g(r)$ and of the three-particle distribution function $g^{(3)}(\mathbf{r},\mathbf{r}')$. The latter only appears in the last term of $L^0(k)$ in Eq. (A7) and of $L_S^0(k)$ in Eq. (A9). These are the only terms in which we introduce a simplifying approximation, based on the use of Kirkwood superposition approximation. As discussed in Ref. [26], this simple scheme to evaluate $L^0(k)$ and $L_S^0(k)$ turns out to be quite effective. In the present context, it also has

the virtue of reducing the need of static inputs of our theory to the previous determination of only $g(r)$ which, as said above, is provided here by the computer simulations. Following this procedure, we then go back to our self-consistent system of equations, Eqs. (3.18)–(3.20), from which we now determine simultaneously $F(k,t)$, $F_S(k,t)$, and $\Delta\zeta^*(t)$. Although the numerical solution of this nonlinear system of equations may be lengthy and is not trivial, it is in fact rather straightforward.

We started by solving Eqs. (3.18)–(3.20) for a variety of interpolating functions within the family in Eq. (3.21). The corresponding solutions for $F(k,t)$ are then compared with the exact (computer simulated) values for this property. We did this by varying the parameters ν and k_C at an arbitrary fixed state, and for a fixed time, representative of the intermediate time regime. After doing this for various times and fixed states, it emerged that the optimum value of the parameters ν and k_C are $\nu=2$ and $k_C=k_{\min}$, where $k_{\min}$ is the position of the first minimum of the static structure factor. In Fig. 1 we illustrate the comparisons involved in this process, for a highly interacting system, $n^*=0.015$, at an intermediate time $t/t_0=5.0$. In Fig. 1(a) we present the results of our theory for $F(k,t)$ as a function of k, for various values of $\nu(=2,6,10)$ keeping k_C fixed at $k_C\sigma=k_{\min}\sigma=1.11$, whereas in Fig. 1(b), we keep fixed $\nu=2$ and vary k_C [$k_C=k_<$, $k_{\max}$, $k_{\min}$, $k_>$, where $k_{\max}\sigma=0.81$ is the position of the main peak of $S(k)$, $k_<\sigma=0.73$ is a wave vector slightly below $k_{\max}$, at which $S(k)\approx1$, and $k_>\sigma=1.6$ is the location of the second maximum of $S(k)$]. From the comparison with the computer simulation results, represented by the symbols, it is clear that the optimum choice of the parameters ν and k_C is indeed $\nu=2$ and $k_C=k_{\min}$. At this point, we adhere to this prescription for the definition of these parameters. Thus, from now on, there is no input of the theory other than $u(r)$ and $g(r)$. Let us now illustrate its application to the same system, but at other time and/or concentration regimes.

In Fig. 2 we present the theoretical results for $F(k,t)$ (solid lines) as applied to the same system but at conditions representative of the regimes of intermediate ($n^*=0.009$) and strong ($n^*=0.015$) coupling. The results in Fig. 2(a) illustrate the behavior of these two conditions at relatively short times, where still the SEXP approximation provides a good representation of the dynamics of the system. For reference, in Figs. 2(a) and 2(b), the SEXP results, obtained from Eq. (3.18) with $\lambda(k)=0$, are also included (dashed lines). Figure 2(b) presents a similar comparison as in Fig. 2(a), but at a longer time, representative of the intermediate-time regime. The general conclusion drawn from this comparison is, on the one hand, that our self-consistent theory provides quite an accurate representation of the time and wave-vector dependence of the intermediate scattering function $F(k,t)$ at the short- and intermediate-time regimes of our system under conditions of weak, intermediate, and strong couplings. Figures 2(a) and 2(b) also illustrate the improvement introduced by our theory over the much simpler, SEXP approximation. The latter, does provide a simple and accurate representation of $F(k,t)$ at low concentrations and short times [16,27], but it fails for moderately to highly correlated systems at intermediate and long times. In the de-
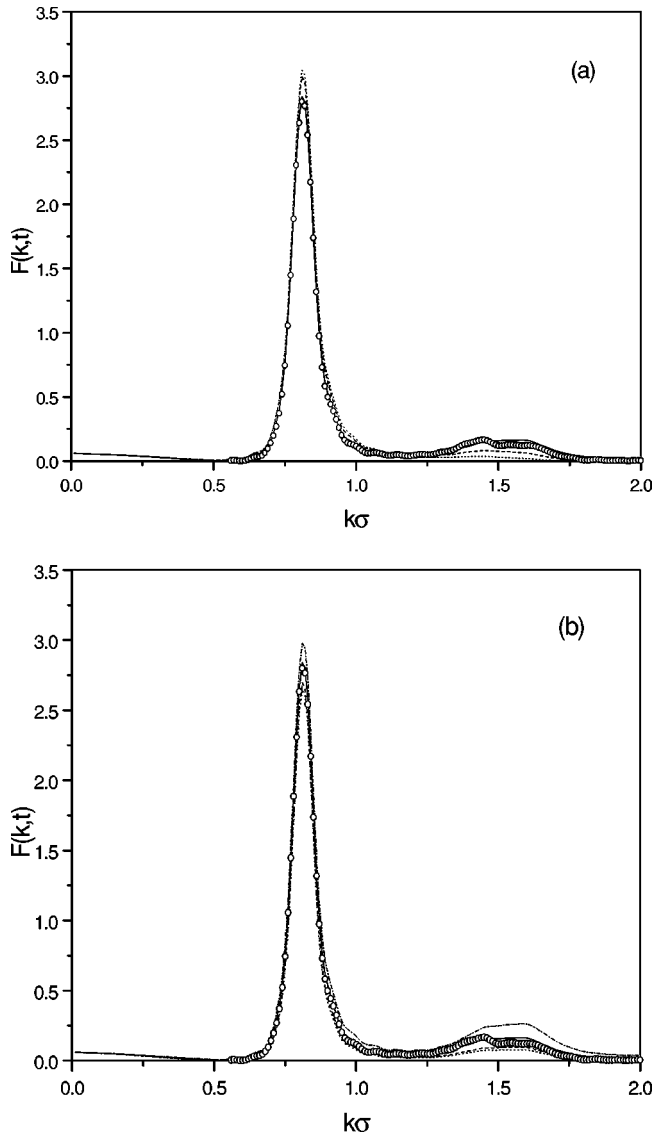
FIG. 1. Intermediate scattering function $F(k,t)$ as a function of the reduced wave vector $k\sigma$, for the Yukawa system [Eq. (4.1)] with $K=500$, $z=0.15$ for $n^*=0.015$ at $t/t_0=5.0$. (a) Comparisons using the interpolating functions $\lambda(k)$ [Eq. (3.21)] with $k_c=k_{\min}$, and $\nu=2$ (solid line), $\nu=6$ (dashed line) and $\nu=10$ (dotted line). (b) Comparisons using the interpolating functions with $\nu=2$ and $k_c=k_<$ (dotted line), $k_c=k_{\max}$ (dashed line), $k_c=k_{\min}$ (solid line) and $k_c=k_>$ (dot-dashed line). Open circles represent the Brownian dynamics (BD) results.
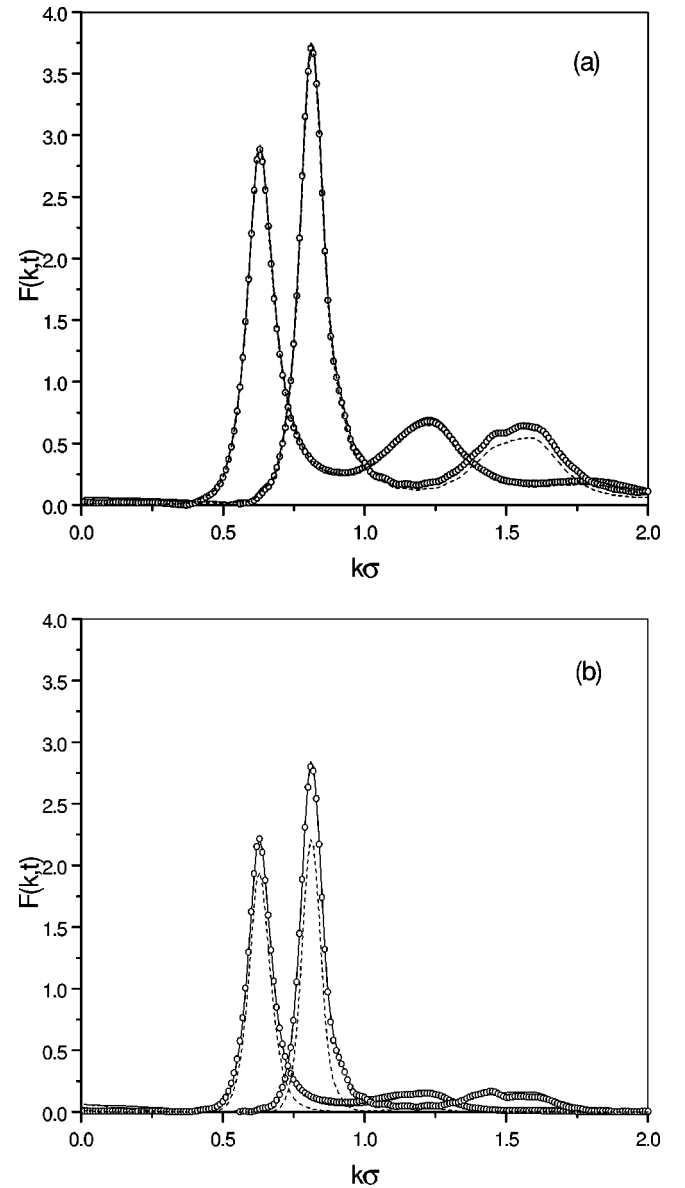
FIG. 2. Intermediate scattering function $F(k,t)$ for the same system as in Fig. 1, but with $n^*=0.009$ (left) and $n^*=0.015$ (right), (a) for $t/t_0=0.83$ (b) for $t/t_0=5.0$. Solid lines represent our theoretical results with parameters with $\nu=2$ and $k_c=k_{\min}$, whereas the Brownian dynamics simulations are represented by the symbols. The results of the single exponential (SEXP) approximation are also included (dashed lines).

velopment of our present theory, this simple approximation served as an important conceptual reference, upon which we elaborated the correction that allowed the proposal of the fully self-consistent scheme in Eqs. (3.18)-(3.20). Figure 2(b) illustrates the extent to which this correction is important at progressively longer times.

To continue with the illustration of the results of our self-consistent theory for the same model system, in Fig. 3 we present the corresponding results for $F(k,t)$ for $n^*=0.009$ at the longest time we considered in the computer simulation. For comparison, Fig. 3 includes $F(k,t)$ at $t/t_0=0$ (i.e., $S(k)$), $t/t_0=13.85$, and $t/t_0=24.93$. Clearly, the high level

of quantitative accuracy of our theory at those relatively long times is again evident from this comparison. For reference, we mention that the SEXP (not shown in this figure), only reproduces qualitatively the time evolution of the main peak of $F(k,t)$, but predicts a much faster decay of its amplitude compared to the simulation results and to the results of our theory, which in Fig. 3 are virtually indistinguishable from each other.

Finally, in Fig. 4 we illustrate the behavior of the intermediate scattering functions under certain limiting conditions. For this, we plot the theoretical results for $-[S(k)/k^2]\ln[F(k,t)/S(k)]$ and $-(1/k^2)\ln[F_S(k,t)]$ as a func-
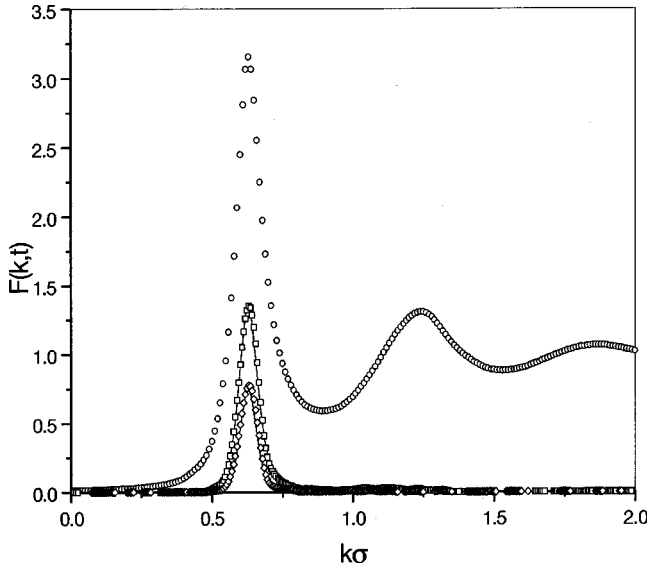
FIG. 3. Theoretical predictions (solid lines) for $F(k,t)$ with parameters $\nu=2$ and $k_c=k_{min}$, for a system with $n^*=0.009$ and $t=0$, $t/t_0=13.85$, and $t/t_0=24.93$. The open circles represents BD results.

tion of t/t_0 for a system with intermediate concentration ($n^*=0.009$), and for values of the wave-vector representative of three regimes: $k\ll k_{max}$, $k\approx k_{max}$ and $k>k_{max}$ [at which $S(k)\approx 1$]. For this system, $k_{max}\sigma=0.63$ is the position of the main peak of $S(k)$, and we select $k_<\sigma=0.02$ and $k_>\sigma=1.10$ as values of the wave vector much less than, and much larger than k_{max} respectively. Notice first that at short times all the curves in Fig. 4 become indistinguishable from each other and from the free-diffusion curve (the straight line with unit slope, see the inset). This reflects the exact short-time limit built in our theory. Notice also another important limit: for all times, $F(k,t)$ should also decay as $F(k,t)=S(k)\exp[-k^2D_0t/S(k)]$ in the limit of small wave vectors. This is illustrated by the results for the collective intermedi-
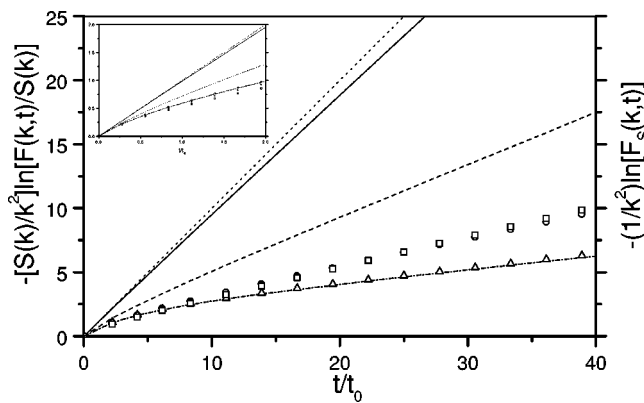

FIG. 4. Theoretical predictions for the intermediate scattering function $F(k,t)/S(k)$ (lines) and $F_S(k,t)$ (symbols) against t/t_0 for the system as in Fig. 3, and three different values of $k\sigma$: $k_<\sigma=0.02$ (solid line and open squares), $k_{max}\sigma=0.63$ (dashed line and open circles), and $k_>\sigma=1.1$ (dot-dashed line and open triangles). The free-diffusion regime is also included (dotted line).

ate scattering function at $k_<\sigma=0.02$. On the other hand, for all wave vectors, $F(k,t)$ and $F_S(k,t)$ are expected to decay exponentially for asymptotically long times, with decay constants $k^2D_0S^{-1}(k)/[1+C(k,z=0)]$ and $k^2D_0/[1+C_S(k,z=0)]$, respectively. Although Fig. 4 only exhibits results for a limited time window, this long-time behavior seems to be already established. Other important features are also apparent in Fig. 4. Thus, for wave vectors very large compared to k_{max}, we expect that the collective and the self-intermediate scattering functions exhibit the same time dependence. Here we illustrate this with the results corresponding to $k_>\sigma=1.10$. Although this value is not much larger than k_{max}, it was chosen such that the static structure factor is unity. Finally, let us notice that at short times, all the data for $-(1/k^2)\ln[F_S(k,t)]$ converge to a single curve. This indicates that at short times $F_S(k,t)$ is Gaussian to a very good approximation. At longer times, however, there is a noticeable dependence of $-(1/k^2)\ln[F_S(k,t)]$ on the wave vector. This concludes the discussion of the application of our self-consistent theory to the specific system employed here with illustrative purpose.

V. SUMMARY AND CONCLUSIONS

In this paper we have presented our proposal for a self-consistent theory of the dynamic properties of a colloidal suspension in the absence of hydrodynamic interactions. This theory was build upon four basic ingredients: (a) the exact results for $F(k,t)$ and $F_S(k,t)$ in terms of a hierarchy of memory functions, as derived from the application of the GLE formalism; (b) the proposal of Vineyard-like connections between $F(k,t)$ and $F_S(k,t)$ through their respective memory functions; (c) an approximate expression for one of these memory functions in terms of the time-dependent friction function $\Delta\zeta(t)$; and (d) a closure relation for $\Delta\zeta(t)$ in terms of $F(k,t)$ and $F_S(k,t)$, also derived within the GLE formalism. As a result, we arrived at the self-consistent system of equations summarized in Eqs. (3.18)–(3.20), and involving only $F(k,t)$, $F_S(k,t)$, and $\Delta\zeta(t)$. The other quantities entering in these equations are static properties that can be written in terms of the radial distribution function $g(r)$ and of the three-particle distribution function $g^{(3)}(\mathbf{r},\mathbf{r}')$ (although, in practice, as explained in the preceding section and in Ref. [26], only $g(r)$ is required in their approximate evaluation). The only element left undetermined in our self-consistent system of equations is the interpolating function $\lambda(k)$ in Eqs. (3.18) and (3.19). When $\lambda(k)=0$, we recover the SEXP approximation. Here, however, we explored a family of interpolating functions $\lambda(k)$ described by Eq. (3.21). In the absence of a more fundamental principle to determine $\lambda(k)$, we proceeded to fix the parameters ν and k_C in Eq. (3.21) by means of the calibration of our theory by comparing its results, for various values of ν and k_C, with the results of a Brownian dynamics computer simulation experiment. For this we choose a simple model system, namely, a two-dimensional Brownian repulsive Yukawa fluid. This allowed us to fix the only element of our self-consistent scheme that was not determined on the basis of physically reasonable arguments, thus leading to our final choice $\nu=2$

and $k_C = k_{\min}$ [where $k\min$ is the location of the first minimum of $S(k)$]. In this manner, our self-consistent theory, represented by Eqs. (3.18)–(3.20) with this choice of ν and k_C, is now a closed system of equations, which only needs the pair potential and the radial distribution function as the only specific static inputs.

In the preceding section we illustrated the quantitative predictive power of our theory by comparing its results with the simulation data for the same model system. As illustrated in Figs. 2 and 3 above, this theory is capable of describing the dynamic properties contained in $F(k,t)$ in a wide range of conditions, involving strongly correlated systems, at the longest times available from our computer simulations.

The presentation of our theory, and its concrete application that served as an illustration, now leave open several important questions. Thus, one would like to know if the choice of the parameters $\nu = 2$ and $k_C = k_{\min}$ happen to be specific for the present system, or if they continue to be a good selection for other systems. We can advance [28] that at least for the three-dimensional version of the present system, this choice of k_C continues to be as good a choice as for the system discussed here, but the optimum value of the parameters ν is $\nu = 6$. At present, however, we cannot identify a meaningful fundamental reason for this fact, neither a compelling reason for a different choice of the interpolating function $\lambda(k)$.

As already stressed above, our theory seems to be highly accurate in its description of the dynamics of strongly correlated systems at long times. Hence, one would expect the same theory to provide a qualitatively accurate description of the phenomenology of the ideal glass transition [20] in strongly correlated systems. As we shall discuss separately [29], this also turns out to be the case. Other aspects on which we shall report shortly, concern the extension of this theory to colloidal mixtures and to systems with strong hydrodynamic interactions. In this paper we only wanted to stress the main physical ideas upon which these developments are being built.

APPENDIX: STATIC PROPERTIES

In this appendix we summarize the essential expressions for the static properties $\chi(k)$, $L^0(k)$, $\chi^S(k)$, and $L_S^0(k)$ associated with $F(k,z)$ and $F_{S(k,z)}$ [see Eqs. (2.1)–(2.4)]. As it was explained in Ref. [22], an adequate description in the diffusive regime can be done in terms of the fluctuations in the local concentration $\delta n(\mathbf{k},t)$, the longitudinal current

$\delta j_l(\mathbf{k},t)$, and the kinetic and configurational components of the stress tensor, $\delta \sigma_K(\mathbf{k},t)$ and $\delta \sigma_U(\mathbf{k},t)$, respectively. In that paper, the microscopic definition of each of these dynamic variables was given, along with their static correlation functions. Here we focus our attention on the configurational component of the stress tensor, defined as

$$\delta \sigma_U(\mathbf{k},t) = \delta \sigma_U'(\mathbf{k},t) + \frac{k_B T}{M} \delta n(\mathbf{k},t), \qquad (A1)$$

where

$$\delta \sigma_U'(\mathbf{k},t) \equiv -\frac{1}{2M\sqrt{N}} \sum_{i=1}^{N} \sum_{j \neq i} \frac{r_{ij}^{\alpha} r_{ij}^{\beta}}{r_{ij}^2} P_k(r_{ij}) e^{i\mathbf{k}\cdot\mathbf{r}_i(t)} - \delta p \qquad (A2)$$

and

$$P_k(r_{ij}) \equiv r_{ij} \frac{du(r_{ij})}{dr_{ij}} \frac{e^{i\mathbf{k}\cdot\mathbf{r}_{ij}(t)} - 1}{\mathbf{k}\cdot\mathbf{r}_{ij}(t)}, \qquad (A3)$$

where $u(r)$ is the interparticle effective pair potential. Since $\chi(k)$ is defined as

$$\chi(k) \equiv \langle \delta \sigma_U(\mathbf{k},0) \delta \sigma_U(-\mathbf{k},0) \rangle, \qquad (A4)$$

we can write

$$\chi(k) \equiv \langle \delta \sigma_U'(\mathbf{k},0) \delta \sigma_U'(-\mathbf{k},0) \rangle - \left(\frac{k_B T}{M} \right)^2 \langle \delta n(\mathbf{k},0)$$
$$\times \delta n(-\mathbf{k},0) \rangle. \qquad (A5)$$

Using Eqs. (A2) and (A3) for the components of $\delta \sigma_U(\mathbf{k},t)$, and remembering that $S(k) \equiv \langle \delta n(\mathbf{k},0) \delta n(-\mathbf{k},0) \rangle$, one can perform the statistical mechanical calculation of the static correlation function $\chi(k)$ to obtain

$$\chi(k) = \left(\frac{k_B T}{m} \right)^2 \left[1 + n \int d\mathbf{r}\, g(r) \frac{\partial^2 \beta u(r)}{\partial z^2} \left(\frac{1 - \cos(kz)}{k^2} \right) \right.$$
$$\left. - \frac{1}{S(k)} \right]. \qquad (A6)$$

On the other hand, as it was pointed out in Ref. [21], $L^0(k)$ is related to the "Markovian" contribution of the configurational memory function $L_{UU}(k,t)$. In that reference, the precise definition of $L^0(k)$ was established [see Eqs. (4.24) and (4.28) of Ref. [21], where $L^0(k)$ is denoted by $L_{UU}^0(k)$], and arguments were given to arrive at the following expression for this quantity in terms of the two- and three-particle distribution function $g(r)$ and $g^{(3)}(\mathbf{r},r')$:

$$M^2\beta^2 L^0(k) = nD_0 \int d^3 r g(r) \frac{\partial^2 \beta u(r)}{\partial z^2}[1 + 2\cos kz] - \frac{D_0 n^2}{k^2}\left[\int d^3 r g(r)\frac{\partial^2 \beta u(r)}{\partial z^2}(1-\cos kz)\right]^2$$

$$+\frac{2D_0 n}{k}\int d^3 r g(r)\frac{\partial^3 \beta u(r)}{\partial z^3}\sin kz + \frac{2D_0 n}{k^2}\int d^3 r g(r)(1-\cos kz)\left[\frac{\partial\nabla\beta u(r)}{\partial z}\right]^2$$

$$+\frac{D_0 n^2}{k^2}\int d^3 r d^3 r' g(\mathbf{r},\mathbf{r}')\{1-2\cos kz+\cos[k(z-z')]\}\left[\frac{\partial\nabla\beta u(r)}{\partial z}\right]\left[\frac{\partial\nabla'\beta u(r')}{\partial z'}\right]. \tag{A7}$$

In a similar way, one can derive the corresponding properties for self-diffusion, $\chi^{(S)}(k)$ and $L_S^0(k)$, with the following results [22]:

$$\chi^{(S)}(k) = \frac{(k_B T/M)^2}{k^2}\left[n\int d\mathbf{r}g(r)\frac{\partial^2 \beta u(r)}{\partial z^2}\right] \tag{A8}$$

and

$$k^2 M^2\beta^2 L_S^0(k) = k^2 D_0\left[n\int d\mathbf{r}g(r)\frac{\partial^2 \beta u(r)}{\partial z^2}\right] - D_0 n^2\left[\int d^3 r g(r)\frac{\partial^2 \beta u(r)}{\partial z^2}\right]^2 + 2D_0 n\int d^3 r g(r)\left[\frac{\partial\nabla\beta u(r)}{\partial z}\right]^2$$

$$+D_0 n^2\int d^3 r d^3 r' g(\mathbf{r},\mathbf{r}')\left[\frac{\partial\nabla\beta u(r)}{\partial z}\right]\left[\frac{\partial\nabla'\beta u(r')}{\partial z'}\right]. \tag{A9}$$

In the equations above, $u(r)$ is the effective interaction pair potential between colloidal particles. Finally, we should repeat that in this paper we have systematically dropped the subindex "UU" employed in Ref. [21], where $\chi(k)$, $\chi^{(S)}(k)$, $L^0(k)$, and $L_S^0(k)$ are denoted, respectively, by $\chi_{UU}(k)$, $\chi_{UU}^{(S)}(k)$, $L_{UU}(k)$, and $L_{UU}^{(S)}(k)$.

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