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Vineyard-like approximations for colloid dynamics

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In this paper we propose a hierarchy of higher-order Vineyard-like approximations for colloidal systems. These consist of approximate expressions for the intermediate scattering function $F(k,t)$ in terms of the *self*-intermediate scattering function $F_s(k,t)$ (or some memory function associated with it), and of other static structural properties of the suspension. In order to assess the accuracy of the proposed approximations, we perform Brownian dynamics simulations in a simple model system (a two-dimensional Yukawa Brownian fluid), in which we determine $F(k,t)$, $F_s(k,t)$, and the required static structural properties. We study proposals for ''second-order'' and ''third-order'' Vineyard-like approximations. We find that the detailed structure of the relationship between the corresponding *collective* and *self* -memory functions turns out to be most important, as quantified by our simulation results.

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I. INTRODUCTION

The intermediate scattering function $F(k,t)$ of a colloidal fluid contains the most relevant information on the dynamic properties of such system [1]. This function is the spatial Fourier transform (FT) of the so-called van Hove function, $G(r,t)$, which 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 [2,3]. Dynamic light scattering allows the experimental determination of this property for colloidal systems [4], just like neutron scattering is employed to determine the same property for an atomic fluid [3]. 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. This function is also amenable to experimental determination by index-matching methods [5]. Hence many of the experimental and theoretical developments in colloid dynamics have aimed at determining and understanding the main features of these dynamic properties [6]. Due to the close analogy with simple liquids, many of these developments have been based on a direct translation to Brownian fluids [7–9], of the corresponding developments in simple atomic liquids [3]. One aspect, however, that has not found a prominent place in colloid dynamics, refers to the intuitive notion that collective dynamics, represented by $F(k,t)$, should be simply related to self-dynamics, represented by $F_S(k,t)$. The simplest proposal for an approximate relation of this sort is referred to as Vineyard approximation [2,3,10], which approximates $F(k,t)$ in terms of $F_S(k,t)$ as

$$F(k,t)=F_S(k,t)S(k), \tag{1.1}$$

where the static structure factor $S(k)$ is the initial value of $F(k,t)$. Although this particular approximation is of very limited value in quantitative applications, for both atomic and colloidal fluids it illustrates the zeroth-order concrete proposal of the notion that collective dynamics can refer to self-dynamics. In fact, this notion was further elaborated in the context of atomic liquids in the early 1970s [3]. Such developments were based on the expressions for $F(k,t)$ and $F_S(k,t)$, derived by statistical mechanical methods, in terms of a hierarchy of memory functions [11]. The idea then was to propose that $F(k,t)$ and $F_S(k,t)$ can be related more accurately to each other through some of their higher-order memory functions, rather than directly. As an illustration, let us consider the fact that $F(k,t)$ and $F_S(k,t)$ can be expressed in terms of their corresponding memory functions $D(k,t)$ and $D_S(k,t)$ through the expresions [3,8]

$$F(k,z)=\frac{S(k)}{z+k^2S^{-1}(k)D(k,z)}, \tag{1.2}$$

$$F_S(k,z)=\frac{1}{z+k^2D_S(k,z)}, \tag{1.3}$$

where $F(k,z)$, $F_S(k,z)$, $D(k,z)$, and $D_S(k,z)$ are the Laplace transforms of $F(k,t)$, $F_S(k,t)$, $D(k,t)$, and $D_S(k,t)$. These equations suggest the proposal of a ''first-order'' Vineyard-like approximation, namely, $D(k,z)=D_S(k,z)$. This leads to a simple explicit expression for $F(k,z)$ in terms of $F_S(k,z)$, namely,

$$F(k,z)=\frac{F_S(k,z)S(k)}{1+nc(k)[zF_S(k,z)-1]}, \tag{1.4}$$

where $nc(k)\equiv1-S^{-1}(k)$. This results in an improvement over the original Vineyard approximation, at least for simple liquids [12]. Still in the context of simple liquids, the same approach was employed to suggest more refined higher-order Vineyard-like approximations [11]. These were based on the derivation of expresions for $D(k,z)$ and $D_S(k,z)$ in terms of

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still higher-order memory functions. Unlike Eqs. (1.1) and (1.4) above, however, such expressions do reflect the details of the underlying microscopic laws that govern the (Newtonian) N-particle dynamics of the atomic fluid, and hence, are not directly applicable to colloidal (i.e., Brownian) fluids. In this work we propose corresponding Vineyard-like approximations for colloidal fluids. For this, in the present paper we shall only keep in mind a monodisperse colloidal suspension in the absence of hydrodynamic interactions, whose microscopic dynamics is governed by the N -particle Langevin equations. In recent work [13], two of the authors carried out a derivation of the most general expressions for $F(k,z)$ and $F_S(k,z)$ in the so-called ''overdamped'' (or *diffusive*) regime, in terms of higher-order memory functions. This regime refers to the times ordinarily probed by dynamic light scattering [and by Brownian dynamics (BD) computer simulations]. Here we use these general expressions as the basis for a proposal of corresponding Vineyard-like approximations for Brownian fluids. In order to test the quantitative accuracy of these proposals, we perform BD computer simulations on a simple model system, namely, a two-dimensional repulsive Yukawa Brownian fluid. This allows us to assess the quantitative accuracy of each of these proposals. The knowledge thus generated allows us to choose the simplest and most accurate one to be employed, for example, in the construction of self-consistent descriptions of the dynamics of colloidal fluids [14].

In Sec. II we consider the general expressions for $F(k,z)$ and $F_S(k,z)$ in terms of their ''third-order'' memory functions, and present five different proposals of Vineyard-like approximations at that level of the hierarchy. In Sec. III we present the results of the quantitative comparisons of these proposals, and compare the results of the best of these third-order approximations with the corresponding results for the lower-order Vineyard-like approximations. In Sec. IV we summarize our conclusions.

II. GENERAL EXPRESSIONS FOR $F(K,T)$ AND $F_S(K,T)$

In previous related work [13,15], the generalized Langevin equation approach, and the concept of the contraction of the description, were 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 a derivation, the assumed underlying microscopic N-particle dynamics was provided by the many-particle Langevin equation. This is just Newton's equation for each of the spherical particles of the suspension, subject to the friction force of the solvent plus the corresponding random force (just as in the ordinary Langevin equation), plus the pairwise direct interactions, derivable from a pair potential $u(r)$. As a result, expressions are derived for $F(k,z)$ in terms of a hierarchy of memory functions, and of static structural properties of the Brownian fluid. 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 the mass and the solvent-friction coefficient of each particle in the suspension, respectively. In the absence of friction ($\zeta^0 \rightarrow 0$), these expressions correspond to those of a simple atomic liquid. 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 ''overdamped,'' limit requires a careful analysis, which was the main subject of Ref. [13]. As a result, one obtains the most general expression for $F(k,t)$ that describes the dynamics of the suspension in the diffusive regime (i.e., for times $t \gg \tau_B$), in which the inertial effects have been damped out by the friction forces, and the only relaxation processes occur through purely diffusive mechanisms. 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. [9], the most general expression for $F(k,z)$ in the diffusive regime can be written as

$$F(k,z)=\cfrac{S(k)}{z+\cfrac{k^2D_0S^{-1}(k)}{1+\cfrac{k^2D_0\chi(k)\chi_{jj}^{-2}}{z+\chi^{-1}(k)L^0(k)+\chi^{-1}(k)\Delta L(k,z)}}}, \tag{2.1}$$

where $D_0 = k_BT/\zeta^0$ is the free-diffusion coefficient of each particle (k_BT being the thermal energy), $S(k)$ is the static structure factor, $\chi_{jj} = k_BT/M$, and $\chi(k)$ is the static correlation function of the fluctuations of the configurational component of the stress tensor of the Brownian fluid. [Note that in Ref. [14], $\chi(k)$, $L^0(k)$, and $\Delta L(k,z)$ carry a subindex ''UU,'' which we shall drop systematically in this paper.] $\chi(k)$ is given by

$$\beta^2M^2\chi(k)=1+n\int d\mathbf{r}\, g(r)\left(\frac{\partial^2\beta u(r)}{\partial z^2}\right)\left(\frac{1-\cos kz}{k^2}\right) - \frac{1}{S(k)}, \tag{2.2}$$

with $\beta=(k_BT)^{-1}$; $u(r)$ is the pair potential of the direct interaction forces, and $g(r)$ the radial distribution function of the Brownian fluid. Thus Eq. (2.1) writes $F(k,z)$ in terms of these properties (which we will assume to be known), and of the memory function $L(k,z) \equiv L^0(k) + \Delta L(k,z)$, which is just the Laplace transform of the time-dependent correlation function of the configurational component of the stress tensor. According to Ref. [13], the Markovian component $L^0(k)$ of $L(k,z)$ can be expressed in terms of D_0 and of purely static properties as

$$M^2\beta^2L^0(k)=n\int d^3r\, g(r)\frac{\partial^2\beta u(r)}{\partial z^2}[1+2\cos kz] - \frac{D_0n^2}{k^2}\left[\int d^3r\, g(r)\frac{\partial^2\beta u(r)}{\partial z^2}(1-\cos kz)\right]^2 + \frac{2D_0n}{k}\left[\int d^3r\, g(r)\frac{\partial^3\beta u(r)}{\partial z^3}\sin kz\right]^2$$

$$+\frac{2D_0 n}{k^2}\int d^3r\, g(r)(1-\cos kz)\left[\frac{\partial \boldsymbol{\nabla} \beta u(r)}{\partial z}\right]^2$$
$$+\frac{D_0 n^2}{k^2}\int d^3r\, d^3r'\, g(\mathbf{r},\mathbf{r}')(1-2\cos kz$$
$$+\cos[k(z-z')])\left[\frac{\partial \boldsymbol{\nabla} \beta u(r)}{\partial z}\right]\cdot\left[\frac{\partial \boldsymbol{\nabla}' \beta u(r')}{\partial z'}\right], \tag{2.3}$$

where $g(\mathbf{r},\mathbf{r}')$ is the three-particle correlation function.

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

$$F_S(k,z)=\cfrac{1}{z+\cfrac{k^2D_0}{1+\cfrac{k^2D_0\chi_S(k)\chi_{jj}^{-2}}{z+\chi_S^{-1}(k)L_S^0(k)+\chi_S^{-1}\Delta L_S(k,z)}}}, \tag{2.4}$$

with

$$\chi_S(k)=\frac{\chi_{jj}^2}{k^2}\left[n\int d\mathbf{r}\, g(r)\frac{\partial^2 \beta u(r)}{\partial z^2}\right] \tag{2.5}$$

and

$$D_0 M^2\beta^2 L_S^0(k)\equiv k^2D_0^2\left[n\int d\mathbf{r}\, g(r)\frac{\partial^2 \beta u(r)}{\partial z^2}\right]$$
$$-D_0^2n^2\left[\int d^3r\, g(r)\frac{\partial^2 \beta u(r)}{\partial z^2}\right]^2$$
$$+2D_0^2 n\int d^3r\, g(r)\left[\frac{\partial \boldsymbol{\nabla} \beta u(r)}{\partial z}\right]^2$$
$$+D_0^2n^2\int d^3r\, d^3r'\, g(\mathbf{r},\mathbf{r}')$$
$$\times\left[\frac{\partial \boldsymbol{\nabla} \beta u(r)}{\partial z}\right]\cdot\left[\frac{\partial \boldsymbol{\nabla}' \beta u(r')}{\partial z'}\right]. \tag{2.6}$$

Equations (2.1) and (2.4) constitute the basis of our proposals for third-order Vineyard-like approximations. They express $F(k,z)$ and $F_S(k,z)$ in terms of purely static properties (assumed known) and of the unknown memory functions $\Delta L(k,z)$ and $\Delta L_S(k,z)$. They also suggest several possible forms to relate $F(k,z)$ with $F_S(k,z)$ through some simple relationships between $\Delta L(k,z)$ and $\Delta L_S(k,z)$. Of course, the most straightforward of such relationships consists of equating $\Delta L(k,z)$ to $\Delta L_S(k,z)$:

$$\Delta L(k,z)=\Delta L_S(k,z). \tag{2.7}$$

This is, however, not the only possible manner to relate $F(k,z)$ and $F_S(k,z)$ through $\Delta L(k,z)$ and $\Delta L_S(k,z)$. In fact, as we shall see in Sec. III, it is not even the most accurate of such relationships. For example, from the manner in which Eqs. (2.1) and (2.4) have been written, we could also propose approximating $\chi^{-1}(k)\Delta L(k,z)$ by its self-counterpart, i.e.,

$$\chi^{-1}(k)\Delta L(k,z)=\chi_S^{-1}(k)\Delta L_S(k,z). \tag{2.8}$$

For some reason, which is not obvious *a priori*, the Vineyard-like approximation defined by this equation turns out to be far more accurate than that defined by Eq. (2.7). In fact, a third version of a simple relationship between $\Delta L(k,z)$ and $\Delta L_S(k,z)$ can be defined through the approximation

$$\frac{\Delta L(k,z)}{L^0(k)}=\frac{\Delta L_S(k,z)}{L_S^0(k)}. \tag{2.9}$$

We can advance that this happens to be the most accurate among these three Vineyard-like approximations defined in terms of simple relationships between $\Delta L(k,z)$ and $\Delta L_S(k,z)$ [i.e., Eqs. (2.7)–(2.9)].

These statements are the results of concrete numerical tests of these approximations when their predictions are compared with the exact results obtained in the computer simulation experiment, as explained in Sec. III. At this point, however, we do not have any obvious *a priori* reason to expect the quantitative superiority of any of these three simple proposals. In fact, these three approximations have in common that the resulting $F(k,t)$ happens to yield the exact short-time expansion up to terms of order t^3, i.e., they all satisfy the exact moment conditions [1,7,9]

$$m^{(0)}(k)=S(k), \tag{2.10}$$

$$m^{(1)}(k)=-k^2D_0, \tag{2.11}$$

$$m^{(2)}(k)=k^4D_0^2+nD_0\int d\mathbf{r}\, g(r)[1-\cos(\mathbf{k}\cdot\mathbf{r})](\mathbf{k}\cdot\boldsymbol{\nabla})^2\beta u(r) \tag{2.12}$$

and

$$m^{(3)}(k)=-k^6D_0^3-3D_0^3k^2n\int d\mathbf{r}\, g(r)(\mathbf{k}\cdot\boldsymbol{\nabla})^2\beta u(r)$$
$$-2D_0^3n\int d\mathbf{r}\, g(r)\sin(\mathbf{k}\cdot\mathbf{r})(\mathbf{k}\cdot\boldsymbol{\nabla})^3\beta u(r)$$
$$-2D_0^3n\int d\mathbf{r}\, g(r)[1-\cos(\mathbf{k}\cdot\mathbf{r})][(\mathbf{k}\cdot\boldsymbol{\nabla})\boldsymbol{\nabla}\beta u(r)]^2$$
$$-D_0^3n^2\int d\mathbf{r}'\, d\mathbf{r}\, g(\mathbf{r},\mathbf{r}')\{1-2\cos(\mathbf{k}\cdot\mathbf{r})$$
$$+\cos[(\mathbf{k}\cdot\mathbf{r}-\mathbf{r}'))]\}(\mathbf{k}\cdot\boldsymbol{\nabla})(\mathbf{k}\cdot\boldsymbol{\nabla}')$$
$$\times(\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}')\beta u(r)\beta u(r'), \tag{2.13}$$

where the moments $m^{(n)}(k)$ of $F(k,t)$ are defined as

$$m^{(n)}(k)=\left(\frac{\partial^n F(k,t)}{\partial t^n}\right)_{t=0}. \tag{2.14}$$

Also, the three approximations in Eqs. (2.7)–(2.9) coincide at large wave vectors since, in that limit, $\chi(k)\approx\chi_S(k)$ and $L^0(k)\approx L_S^0(k)$.

The short-time limit of $F(k,z)$ and $F_S(k,z)$ is particularly interesting, since the contribution of $\Delta L(k,z)$ and $\Delta L_S(k,z)$ only appears in the terms of order t^4 and higher, in the short-time expansion of $F(k,t)$ and $F_S(k,t)$. In fact, if we set $\Delta L(k,z)=0$ in Eq. (2.1), we obtain a simple, closed approximation for $F(k,z)$, namely,

$$F(k,z)=\frac{S(k)}{z+\dfrac{k^2D_0S^{-1}(k)}{1+\dfrac{k^2D_0\chi(k)\chi_{jj}^{-2}}{z+\chi^{-1}(k)L^0(k)}}}, \tag{2.15}$$

and similarly, for $F_S(k,t)$,

$$F_S(k,z)=\frac{1}{z+\dfrac{k^2D_0}{1+\dfrac{k^2D_0\chi_S(k)\chi_{jj}^{-2}}{z+\chi_S^{-1}(k)L_S^0(k)}}}. \tag{2.16}$$

Equations (2.15) and (2.16) coincide with the so-called single exponential memory (SEXP) approximation, originally suggested and applied by Arauz-Lara and Medina-Noyola [9]. Equation (2.16) has been widely employed to interpret the self-diffusion properties of model experimental and simulated colloidal systems [16,17]. However, most such applications deal with rather dilute systems and/or with relatively short times; in the oposite regime (highly interacting systems at much longer times), the limitations of this simple approximation are much more apparent. This is also true for the SEXP approximation of the *collective* intermediate scattering function in Eq. (2.15), as recently discussed in Ref. [18]. The structure of the general expression for $F(k,z)$ and $F_S(k,z)$ in Eqs. (2.1) and (2.4) suggest, however, that the SEXP approximation might serve as a good initial reference to construct higher-order Vineyard-like approximations, in which $\Delta L(k,z)$ and $\Delta L_S(k,z)$ are not neglected. For this, let us rewrite the general expressions for $F(k,z)$ and $F_S(k,z)$ in Eqs. (2.1) and (2.4) as

$$F(k,z)=\frac{S(k)}{z+\dfrac{k^2D_0S^{-1}(k)}{1+C(k,z)}} \tag{2.17}$$

and

$$F_S(k,z)=\frac{1}{z+\dfrac{k^2D_0}{1+C_S(k,z)}}, \tag{2.18}$$

with

$$C(k,z)=\frac{k^2D_0\chi(k)\chi_{jj}^{-2}}{z+\chi^{-1}(k)L^0(k)+\chi^{-1}(k)\Delta L(k,z)} \tag{2.19}$$

and

$$C_S(k,z)=\frac{k^2D_0\chi_S(k)\chi_{jj}^{-2}}{z+\chi_S^{-1}(k)L_S^0(k)+\chi_S^{-1}(k)\Delta L_S(k,z)}. \tag{2.20}$$

Clearly, the SEXP approximation corresponds to setting $\Delta L(k,z)=\Delta L_S(k,z)=0$, i.e., in approximating $C(k,z)$ and $C_S(k,z)$, respectively, by

$$C(k,z)=C^{SEXP}(k,z)\equiv\frac{k^2D_0\chi(k)\chi_{jj}^{-2}}{z+\chi^{-1}(k)L^0(k)} \tag{2.21}$$

and

$$C_S(k,z)=C_S^{SEXP}(k,z)\equiv\frac{k^2D_0\chi_S(k)\chi_{jj}^{-2}}{z+\chi_S^{-1}(k)L_S^0(k)}. \tag{2.22}$$

Let us now write Eqs. (2.19) and (2.20) as

$$C(k,z)=C^{SEXP}(k,z)+\Delta C(k,z) \tag{2.23}$$

and

$$C_S(k,z)=C_S^{SEXP}(k,z)+\Delta C_S(k,z). \tag{2.24}$$

This allows us to suggest our fourth Vineyard-like approximation, namely,

$$\Delta C(k,z)=\Delta C_S(k,z). \tag{2.25}$$

Equations (2.17) and (2.18), along with this equation, establish our fourth proposal for an approximate relationship between $F(k,z)$ and $F_S(k,z)$, this time through the memory functions $\Delta C(k,z)$ and $\Delta C_S(k,z)$, defined in Eqs. (2.23) and (2.24). Just like our previous proposals, this approximation is also exact at short times, up to terms of order t^3. Furthermore, it is also equivalent to an approximate (but rather involved and not very illuminating) expression for $\Delta L(k,z)$ in terms of $\Delta L_S(k,z)$.

To conclude our presentation of the various proposals for Vineyard-like approximations that use the full information in the general results in Eqs. (2.1) and (2.4), let us note that Eqs. (2.23) and (2.24) could also be written as

$$C(k,z)=C^{SEXP}(k,z)[1+\Delta C^*(k,z)] \tag{2.26}$$

and

$$C_S(k,z)=C_S^{SEXP}(k,z)[1+\Delta C_S^*(k,z)], \tag{2.27}$$

with

$$\Delta C^*(k,z)\equiv\frac{\Delta C(k,z)}{C^{SEXP}(k,z)} \tag{2.28}$$

and

$$\Delta C_S^*(k,z)\equiv\frac{\Delta C_S(k,z)}{C_S^{SEXP}(k,z)}. \tag{2.29}$$

This suggests a fifth possible proposal to relate $\Delta L(k,z)$ with $\Delta L_S(k,z)$, namely,

$$\Delta C^*(k,z)=\Delta C_S^*(k,z). \tag{2.30}$$

This equation, along with Eqs. (2.17)–(2.24), defines a fifth means by which to relate $F(k,z)$ and $F_S(k,z)$, which is also equivalent to an approximate relationship between $\Delta L(k,z)$ and $\Delta L_S(k,z)$, namely,

$$\frac{\chi^{-1}(k)\Delta L(k,z)}{z+\chi^{-1}(k)L^0(k)+\chi^{-1}(k)\Delta L(k,z)} = \frac{\chi_S^{-1}(k)\Delta L_S(k,z)}{z+\chi_S^{-1}(k)L_S^0(k)+\chi_S^{-1}(k)\Delta L_S(k,z)}. \tag{2.31}$$

Let us advance here that this proposal happens to be virtually as accurate as our third proposal above, defined by Eq. (2.9). The reason for this can be understood if we write Eq. (2.31) as

$$\frac{\Delta L^*(k,z)}{1+\dfrac{z}{z_I(k)}+\Delta L^*(k,z)} = \frac{\Delta L_S^*(k,z)}{1+\dfrac{z}{z_I^{(S)}(k)}+\Delta L_S^*(k,z)}, \tag{2.32}$$

with

$$\Delta L^*(k,z) \equiv \frac{\Delta L(k,z)}{L^0(k)} \tag{2.33}$$

and

$$\Delta L_S^*(k,z) \equiv \frac{\Delta L_S(k,z)}{L_S^0(k)}, \tag{2.34}$$

and with $z_I(k) \equiv \chi^{-1}(k)L^0(k)$ and $z_I^{(S)}(k) \equiv \chi_S^{-1}(k)L_S^0(k)$. Clearly, $z_I^{-1}(k)$ and $z_I^{(S)-1}(k)$ are the relaxation times of the memory functions $C^{SEXP}(k,z)$ and $C_S^{SEXP}(k,z)$, respectively. In the short-time, large-wave-vector regime, we have that $z/z_I(k) \approx z/z_I^{(S)}(k) \gg 1$, and hence, Eq. (2.30) is consistent with

$$\Delta L^*(k,z)=\Delta L_S^*(k,z), \tag{2.35}$$

which is Eq. (2.9). In the oposite regime, i.e., long times, $z/z_I(k)$ and $z/z_I^{(S)}(k)$ can be neglected compared to 1 in Eq. (2.32), which is then also consistent with Eq. (2.35). Thus we can expect our fifth proposal [Eq. (2.30)] to lead to similar predictions to our third proposal [Eq. (2.9)] [which can be rewritten as Eq. (2.35) above].

In summary, here we have defined five different manners to propose approximate relationships between $F(k,z)$ and $F_S(k,z)$, in terms of corresponding relationships between the third-order memory functions $\Delta L(k,z)$ and $\Delta L_S(k,z)$ entering in the general expressions for $F(k,z)$ and $F_S(k,z)$ in Eqs. (2.1) and (2.4). These five Vineyard-like approximations were suggested by the various possible manners of writing the latter equations, and their respective quantitative accuracy cannot be assessed *a priori*. Thus, in what follows, we shall subject these approximations to a quantitative test that will allow us to discriminate among them. This is done with the assistance of exact (i.e., simulated) data for both $F(k,z)$ and $F_S(k,z)$ obtained for a particular model system, namely, a two-dimensional Yukawa Brownian fluid.

III. NUMERICAL COMPARISONS

Let us consider a simple model system of a monodisperse Brownian fluid without hydrodynamics interactions. Since all we need is some form of indication of the quantitative accuracy of the various Vineyard-like approximations just defined, we shall choose a particularly simple model system, namely, a two-dimensional Yukawa Brownian fluid. This consists of N Brownian particles in an area A, which undergo Brownian motion governed by the overdamped N-particle Langevin equations [19]

$$\frac{d\mathbf{r}_i(t)}{dt}=\beta D_0\mathbf{f}_i(t)+\beta D_0\mathbf{F}_i(t) \quad (i=1,2,\ldots,N), \tag{3.1}$$

where $\mathbf{f}_i(t)$ is the random force with zero mean and time-dependent correlation funcion given by $\langle f_i^{(\alpha)}(t)f_j^{(\beta)}(0)\rangle = \delta_{\alpha\beta}\delta_{ij}k_BT\zeta^0 2\,\delta(t)$, and where $\mathbf{F}_i(t)$ is the force on particle i due to its direct interactions with the other $(N-1)$ particles in the system. $\mathbf{F}_i(t)$ is assumed to be pairwise additive, with the pairwise forces derivable from a potential $u(r)$. We shall consider a repulsive Yukawa potential, which we will write as

$$\beta u(r)=\begin{cases} K\dfrac{e^{-z(r-1)}}{r}, & r>1 \\ \infty, & r<1. \end{cases} \tag{3.2}$$

Here we have added a physically irrelevant hard-core interaction, with hard-core diameter σ taken as unity, and will fix the parameters K and z at the values $K=500$ and $z=0.15$. There is no special reason for this selection, other than the fact that this model system has been studied extensively elsewhere [17]. Our Brownian dynamics simulation employs the Ermack-McCammon algorithm to solve Eq. (3.1) numerically, and we refer the reader to Refs. [19] for details.

From our simulation experiment, we determine the radial distribution function $g(r)$, from which we calculate the static structure factor, and the various static properties referred to in Sec. II [see Eqs. (2.2), (2.3), (2.5), and (2.6)]. The only approximation we introduced in such calculations refers to the superposition approximations for the three-particle distribution function $g(\mathbf{r},\mathbf{r}')$ appearing in the last terms of Eqs. (2.3) and (2.6), which we show elsewhere [18] to be a reasonable approximation. In addition, we also simulate both $F(k,t)$ and $F_S(k,t)$. From our results for $F_S(k,t)$, we extract $\Delta L_S(k,z)$ according to Eq. (2.1) [or, equivalently, $\Delta C_S(k,z)$, according to Eq. (2.18)], to be used as an input in each of the five versions of the Vineyard-like approximations for $F(k,t)$. The resulting values for $F(k,t)$ are then compared with each other, and with the exact values of this property obtained directly from the simulation. We carried out this exercise for various values of the reduced bulk concentrations $n^*=(N/A)\sigma^2$, ranging from moderately interacting ($n^*=0.003$) to highly interacting ($n^*=0.012$) conditions, as illustrated in Fig. 1, where we present the radial distribution

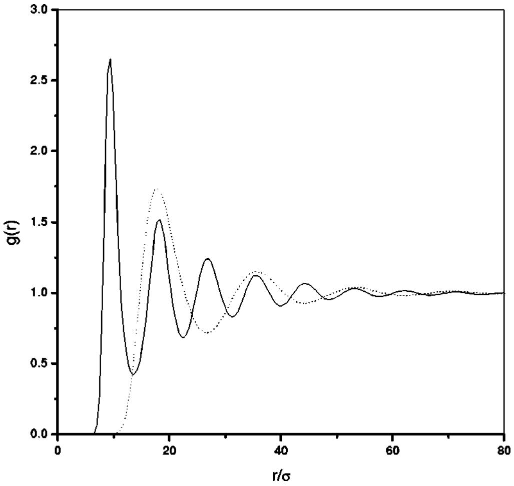

FIG. 1. Radial distribution function $g(r)$ for a system with potential parameters $K=500$ and $z=0.15$. The reduced bulk concentrations are $n^*=0.003$ (dotted line) and $n^*=0.012$ (solid line).

function $g(r)$ obtained in our BD simulations for the lowest and highest of these concentrations.

The data of the type in Fig. 1 allow us to calculate exactly the value of all the static properties referred to in Sec. II, namely, $\chi(k)$, $\chi^{(S)}(k)$, $L^0(k)$, and $L_S^0(k)$ [except for the term involving $g^{(3)}(\mathbf{r},\mathbf{r}')$, which we approximate by its superposition approximation]. In particular, we calculate the static structure factor $S(k)$, which is the initial value of the intermediate scattering function $F(k,t)$. In Fig. 2 we plot $S(k)=F(k,t=0)$ (solid line) for an intermediate but strongly correlated system ($n^*=0.009$). Figure 2 serves to illustrate the main features of the time evolution of $F(k,t)$. For this, in this figure we have also included $F(k,t)$ for latter times, namely, $t=13.88t_0$ and $55.55t_0$ (with $t_0\equiv\sigma^2/D_0$ being a rather arbitrary time unit, representing the time it takes one particle to diffuse its hard-sphere diameter). From Fig. 2 we immediately learn the most important feature of the dynamic evolution of $F(k,t)$. This refers to the fact that the entire initial (static) stucture of the fluid, represented by $S(k)=F(k,t=0)$, is washed away rather quickly (i.e., it decays to almost zero already for times $t/t_0\approx 10$) for most wave vectors, except for those near the position $k_{\max}$ of the main peak of $S(k)$. As we see in Fig. 2, at longer times it is only $F(k\approx k_{\max},t)$ which survives from the original structure in $S(k)$; i.e., for $t\approx 50t_0$ $F(k,t)/S(k)$ is already negligible for all wave vectors, except for $k\approx k_{\max}$, where $F(k_{\max},t)$ has only decayed to about 10% its initial value.

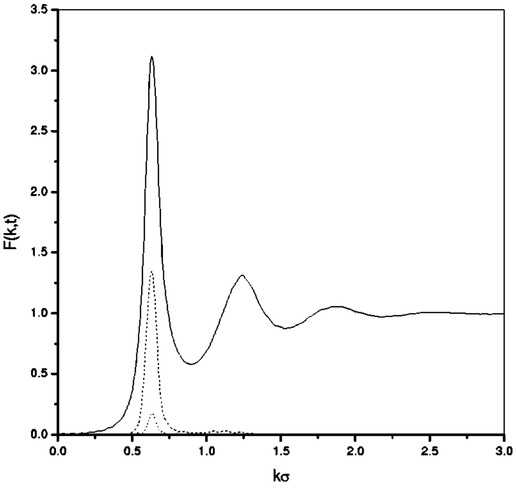

FIG. 2. Intermediate scattering function $F(k,t)$ for a system with the same potential parameters as in Fig. 1: $n^*=0.009$ and $t=0$ (solid line), $t=13.88t_0$ (dashed line), and $t=55.55t_0$ (dotted line).

This observation suggests that the most stringent test of any approximate theory of the dynamic evolution of $F(k,t)$ is the comparison with the exact (simulated) data for $F(k_{\max},t)/S(k_{\max})$. These data are presented (circles) in Fig. 3 for the concentrations $n^*=0.003$, 0.009, and 0.012. In this figure we also illustrate the main results of this paper, namely, the predictions of the five Vineyard-like approximations defined in Sec. II, and its comparison with the corresponding exact data for $F(k_{\max},t)/S(k_{\max})$. Let us comment upon the most salient features of this comparison. As illustrated in Fig. 3(a), at low concentrations all these approximations provide an excellent description of the time evolution of $F(k_{\max},t)$. This is particularly true for the initial decay of $F(k_{\max},t)/S(k_{\max})$, but also for a longer time window ($0\leqslant t\lesssim 20\ t_0$). In fact, Fig. 3(a) does not provide strong quantitative elements to discriminate among the various proposals for these Vineyard-like approximations. One might think that what happens at these small concentrations is that the contribution $\Delta L(k,z)$ to the configurational stress-tensor correlation function is actually very small, and hence, the differences between all the approximations considered should also be small at low concentrations. If this were the case, however, all the various approximations would converge to the SEXP approximation, corresponding precisely to the condition $\Delta L(k,z)=0$. In order to check this, in Fig. 3(a) we also include the result of the SEXP approximation. There we can see that the short-time regime, where the SEXP results coincide with the exact data, corresponds to a rather narrow time window [$0\leqslant t\lesssim 5t_0$ in Fig. 3(a)] within which $F(k_{\max},t)$ has decayed to about 70% of its initial value. Of course, in this short-time regime, all our five proposed approximations indeed coincide with the SEXP and with the simulation data. For latter times, however, the SEXP departs more significantly from the exact data than any of our proposals involving $\Delta L(k,z)\neq 0$.

Although a closer look at Fig. 3(a) could actually reveal some quantitative features that are indeed relevant, these are the ones which are dramatically amplified at higher concentrations, as illustrated in Figs. 3(b) and 3(c). First let us note that in these figures the discrepancy among the various approximations is now much larger. Also note that the expected short-time agreement is now restricted to an extremely short-time window. The comparison in Figs. 3(b) and 3(c) do provide strong elements to discriminate among the five proposed approximations. Clearly, the most important conclusion drawn from the results in these figures is that the most accurate approximations are those in which we approximate either $\Delta L^*(k,z)=\Delta L_S^*(k,z)$ [i.e., Eq. (2.33)] or $\Delta C^*(k,z)=\Delta C_S^*(k,z)$ [i.e., Eq. (2.28)]. In fact, also surprisingly, the numerical results of both of these approximations are virtually indistinguishable from each other in the scales of Fig. 3. The reason for this coincidence was already advanced in Sec. II [see the discussion after Eq. (2.29)]. From

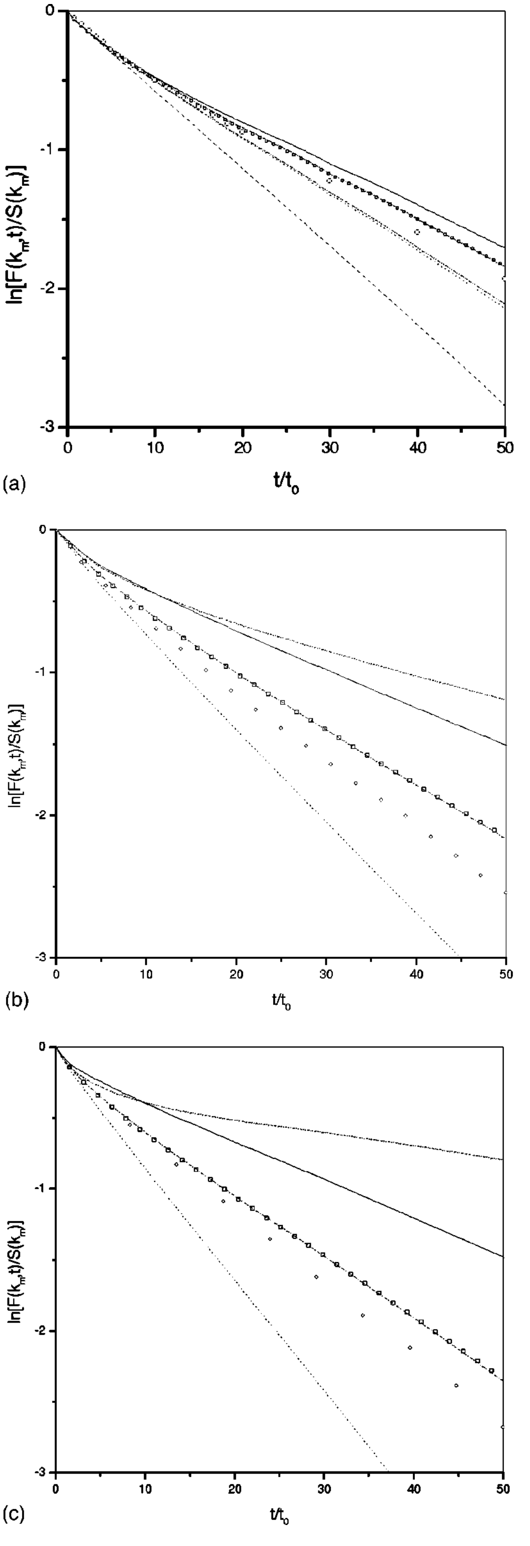

FIG. 3. Semilogarithmic plots of $F(k_{max},t)/S(k_{max})$ for a system with the same potential parameters as in Fig. 1. (a) $n^* = 0.003$ and $k_{max}\sigma = 0.37$. (b) $n^* = 0.009$ and $k_{max}\sigma = 0.63$. (c) $n^* = 0.012$ and $k_{max}\sigma = 0.72$. In this figure the open circles represent BD results, and the five Vineyard-like approximations are shown by the solid line for $\Delta C(k,z) = \Delta C_S(k,z)$, the solid line and squares for $\Delta C^*(k,z) = \Delta C_S^*(k,z)$, the dotted line for $\chi^{-1}\Delta L(k,z) = \chi_S^{-1}\Delta L_S(k,z)$, the dash-dotted line for $\Delta L^*(k,z) = \Delta L_S^*(k,z)$, and the dash-dot-dotted line for $\Delta L(k,z)$. In (a), the dashed line represents the SEXP approximation.

Figs. 3(b) and 3(c) we also learn the quantitative importance of the specific property that we choose to build a given Vineyard-like approximation. Thus, to our surprise, the ''simplest'' proposal, namely, that based on approximating the ''bare'' memory function $\Delta L(k,z)$ by its self-counterpart, turns out to be the least accurate, and most erratic approximation at high concentrations. These negative features are corrected when we employ not $\Delta L(k,z)$, but $\chi^{-1}(k)\Delta L(k,z)$, as the basis of our Vineyard-like approximation [Eq. (2.8)]. Although at small concentrations there is no need for this correction [see Fig. 3(a)], at larger concentrations it leads to much more accurate and systematic quantitative results. Note, in fact, that these results always lie below the simulation data, i.e., they somewhat overestimate the relaxation of $F(k_{\max},t)$. In contrast, if we normalize $\Delta L(k,z)$ not with $\chi(k)$ but with $L^0(k)$, and choose the dimensionless property $\Delta L^*(k,z) \equiv \Delta L(k,z)/L^0(k)$ as the basis of our Vineyard-like approximation [i.e., Eq. (2.33)], the corresponding results are systematically above the simulation data for $F(k_{\max},t)/S(k_{\max})$. As mentioned above, this turns out to be the most accurate approximation, and part of the reason for this can be found in the use of a dimensionlesss property such as $\Delta L^*(k,z)$ as the basis of the approximation. A similar comment could also be made regarding the Vineyard-like approximations in Eqs. (2.25) and (2.28). In this case, both are based on dimensionless properties, namely, $\Delta C(k,z)$ and $\Delta C^*(k,z) \equiv \Delta C(k,z)/C^{SEXP}(k,z)$. For reasons explained above, however, the latter turns out to be virtually identical to the approximation based on $\Delta L^*(k,z)$, and, together with this, it is the most accurate proposal. In contrast, the former systematically underestimates the relaxation of $F(k_{\max},t)$.

Let us now compare the results in Fig. 3, for the decay of $F(k,t)/S(k)$ at $k = k_{\max}$, with the results in Fig. 4, corresponding to other values of k, namely, $k_-\sigma = 0.65$ [Fig. 4(a)] and $k_+\sigma = 1.03$ [Fig. 4(b)]. k_- is such that $k_-\sigma < k_{\max}\sigma = 0.72$ and $S(k_-) \approx 1$, whereas k_+ is such that $k_+ > k_{\max}$, and it coincides approximately with the location of the first minimum of the static structure factor. As we can see if we compare these figures with Fig. 3(c), the dispersion of the results of the various approximations around the exact data is less severe for $k \neq k_{\max}$, especially for wave vectors larger than $k_{\max}$. In fact, even the most primitive Vineyard-like approximation [based on the bare $\Delta L(k,z)$] performs well at these wave vectors. Also here, there is an almost exact quantitative coincidence between the results based on $\Delta L^*(k,z)$ and those based on $\Delta C^*(k,z)$.

The results in Fig. 4 confirm that these two are the most accurate of the proposals for Vineyard-like approximations based on the full expressions in Eqs. (2.1) and (2.4) for $F(k,z)$ and $F_s(k,z)$ in terms of the third-order memory functions $\Delta L(k,z)$ and $\Delta L_s(k,z)$. Thus in the hierarchical sense in which Vineyard's approximation [Eq. (1.1)] is the zeroth order approximation [Eq. (1.1)], and Eq. (1.4), based on the (''first-order'') memory functions $D(k,z)$ and $D_s(k,z)$ is the first-order approximation, we can say that the five approximations discussed so far are variants of third-order Vineyard-like approximations. Second-order approximations could also be considered, and these would be based on the ''second-order'' memory functions $C(k,z)$ and $C_s(k,z)$ in Eqs. (2.17) and (2.18). If we compare these equations with

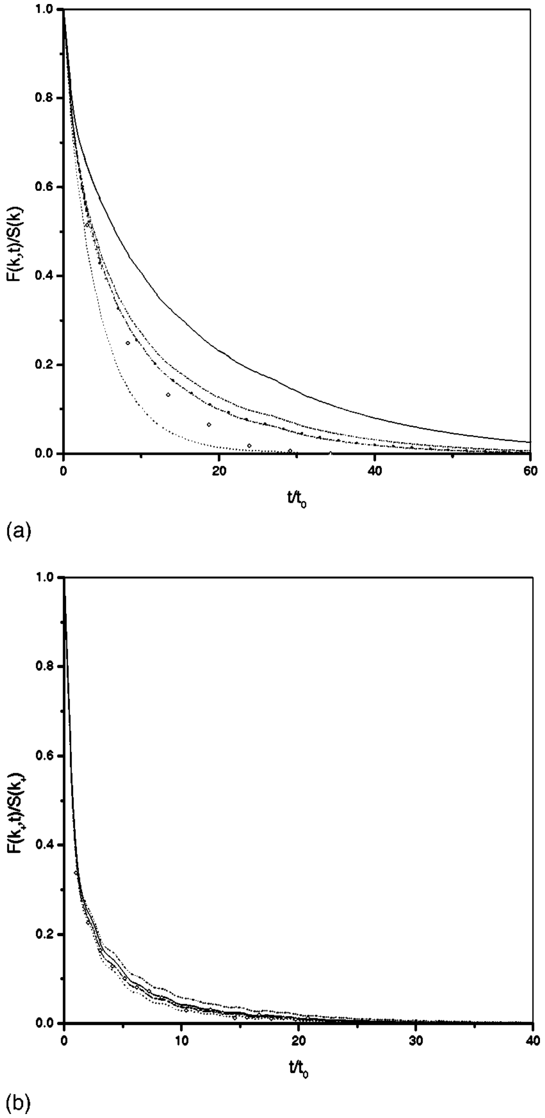

FIG. 4. $F(k,t)/S(k)$ for a system with the same potential parameters as in Fig. 1, where $n^*=0.012$. (a) $k_-\sigma=0.65$. (b) $k_+\sigma=1.03$. The open circles and Vineyard-like approximation lines are as in Fig. 3.

Eqs. (1.2) and (1.3), we have that $D(k,z)=[1+C(k,z)]^{-1}$ and $D_S(k,z)=[1+C_S(k,z)]^{-1}$. Thus simply setting $C(k,z)=C_s(k,z)$ is actually equivalent to approximating $D(k,z)=D_S(k,z)$, which leads to the first-order Vineyard-like approximation in Eq. (1.4). Thus we need more detailed information on the actual structure of $C(k,z)$ and $C_s(k,z)$. The most detailed structure of these memory functions is provided by the full expressions for $F(k,t)$ and $F_S(k,t)$ in Eqs. (2.1) and (2.4), or equivalently, in Eqs. (2.19) and (2.20). For our purpose, however, let us ignore all the detailed structures of $C(k,z)$ and $C_s(k,z)$ in Eqs. (2.19) and (2.20), except for the initial values $C(k,t=0)=k^2D_0\chi(k)$ and $C_s(k,t=0)=k^2D_0\chi_s(k)$, and write

$$C(k,z)=k^2D_0\chi(k)H(k,z) \tag{3.3}$$

and

$$C_S(k,z)=k^2D_0\chi_S(k)H_S(k,z). \tag{3.4}$$

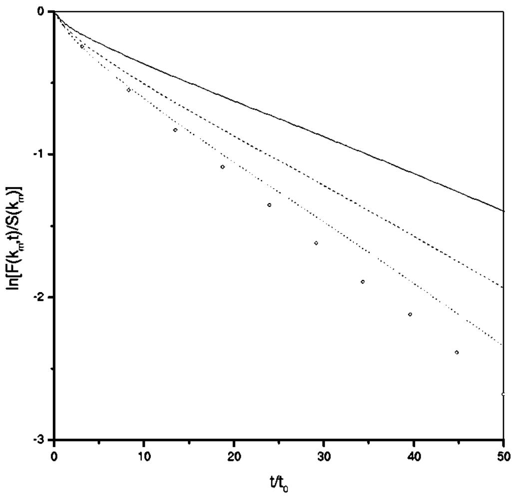

FIG. 5. Semilogarithmic plot of $F(k_{max},t)/S(k_{max})$ for a system with the same potential parameters as in Fig. 1: $n^*=0.012$ and $k_{max}\sigma=0.72$. Open circles represent BD results, and the Vineyard-like approximations are shown by the solid line for $C(k,z)=C_S(k,z)$, the dashed line for $H(k,z)=H_S(k,z)$, and the dotted line for $\Delta L^*(k,z)=\Delta L_S^*(k,z)$.

This suggests the second-order Vineyard-like approximation $H(k,z)=H_S(k,z)$, which can also be written as

$$\chi^{-1}(k)C(k,z)=\chi_s^{-1}(k)C_s(k,z). \tag{3.5}$$

In Fig. 5 we compare the results of this approximation with those of the first-order approximation in Eq. (1.4) and of the best third-order approximaions discussed in Sec. II, namely, Eqs. (2.33) and (2.28).

The comparison in Fig. 5 illustrates the expected fact that the quantitative accuracy of these approximations increases with the level of the memory function involved. Figure 5 corresponds to the most demanding conditions, namely, $k=k_{\max}$, for the highest concentration $n^*=0.012$. Let us close this section by saying that all the conclusions of this section, mostly illustrated for strongly correlated systems, are systematically confirmed at lower concentrations as well.

IV. SUMMARY

In this paper we have presented a hierachy of Vineyard-like approximations, based on approximating the collective memory function of a given order by its corresponding self-memory function. The zeroth-order approximation is the Vineyard approximation itself, $F(k,t)=F_S(k,t)S(k)$, which only satisfies the zeroth moment condition, and does not distinguish between Brownian and Newtonian dynamics. The first-order approximation consists of approximating the first-order memory funciton $D(k,z)$ in Eq. (1.2) by its self-counterpart $D_S(k,z)$, thus leading to Eq. (1.4). This approximation for $F(k,t)$ satisfies the zeroth and the first moment conditions in Eqs. (2.10) and (2.11) [provided that $F_S(k,t)$ does satisfy the corresponding conditions]. The second-order Vineyard-like approximation is defined by Eqs. (2.17) and (2.18), together with Eq. (3.5) above. This satisfies up to the second moment condition in Eq. (2.12). Finally, for the level involving the third-order memory functions $\Delta L(k,z)$ and $\Delta L_S(k,z)$, we studied five different proposals. All of them are such that the resulting Vineyard-like approximation uses the full structure of the general expressions for $F(k,z)$ and $F_S(k,z)$ in Eqs. (2.1) and (2.4). Furthermore, all of them satisfy the exact third moment condition in Eq. (2.13). The main difference was the specific manner in which $\Delta L(k,z)$ and $\Delta L_S(k,z)$ were related. In the absence of a reliable argument to discriminate among these five proposals, we resorted to a quantitative comparision in the context of the properties of a simple specific model system. This allowed us to discriminate among these five third-order alternatives. Surprisingly enough, two of these five proposals happened to yield virtually indistinguishable results, which also happened to be systematically the most accurate. The first of these two approximations is defined by Eqs. (2.1) and (2.4), along with Eq. (2.9). The second is defined by Eqs. (2.17), (2.18), (2.25), and (2.27), along with Eq. (2.30). From a quantitative point of view, either of these two approximations constitute the best representative of the third-order Vineyard-like approximation. Their results are far better than any of the other approximations of the kind considered here, both at the same level and at lower levels in the hierarchy discussed in the present work. We expect that the information just summarized will be useful in an analysis of experimental or simulated results on more realistic models than the one considered here. For the time being, this information is being employed in the development of a self-consistent theory to colloid dynamics, but this will be reported separately [14].

ACKNOWLEDGMENTS

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