Nonexponential relaxation of density fluctuations in charge-stabilized colloids

Peter Baur, Gerhard Nägele,* and Rudolf Klein

Fakultät für Physik, Universität Konstanz, Postfach 5560, D-78434 Konstanz, Germany

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The relaxation of density fluctuations in charge-stabilized colloidal suspensions is characterized by the dynamic structure factor $S(q,t)$, which can be measured by dynamic light scattering. Whereas the short-time behavior of this quantity is well understood, its characteristics at longer times are more difficult to determine due to memory effects, which lead to a nonexponential decay of $S(q,t)$. A suitable measure of the overall nonexponential decay of $S(q,t)$ is the reduced memory function $\Delta(q)$. Formally exact results for $\Delta(q)$ can be obtained on the basis of the many-body Smoluchowski equation, but for its evaluation one has to introduce approximations. Earlier calculations of $\Delta(q)$ based on a particular form of the mode-coupling approximation were found to be in qualitative disagreement with experimental results. In particular, for monodisperse suspensions it was predicted that $\Delta(q\to0)=0$, whereas positive values for $\Delta(0)$ are extrapolated from experimental data. It will be shown that surprisingly small amounts of polydispersity can give rise to finite values of the measured reduced memory function at $q=0$. For this reason, we have improved the mode-coupling approximation and extended the theory to moderately polydisperse suspensions. Our results are in good qualitative agreement with available experimental data. We have also studied how the nonexponential decay of $S(q,t)$ is affected by the amount of added electrolyte. The reduced memory function is found to depend significantly on the ionic strength. [S1063-651X(96)08405-9X]

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I. INTRODUCTION

Since the invention of dynamic light scattering (DLS) techniques, one has been able to determine the dynamic structure factor of colloidal suspensions over a wide range of time and length scales [1,2]. The dynamic structure factor $S(q,t)$ of monodisperse suspensions is the autocorrelation function of microscopic density fluctuations, i.e.,

$$S(q,t)=\frac{1}{N}\langle \delta c(\mathbf{q},t)\delta c(-\mathbf{q},0)\rangle, \tag{1}$$

where $\delta c(\mathbf{q},t)=c(\mathbf{q},t)-\langle c(\mathbf{q},t)\rangle$ and

$$c(\mathbf{q},t)=\sum_{l=1}^{N} e^{-i\mathbf{q}\cdot\mathbf{R}_l(t)} \tag{2}$$

is the Fourier component of the microscopic particle density $c(\mathbf{r},t)$. Here $\mathbf{R}_l(t)$ denotes the position vector of the lth colloidal particle, $\mathbf{q}$ is the scattering wave vector of modulus q, N is the number of particles in the scattering volume Ω, and $\langle \rangle$ denotes the canonical ensemble average. The function $S(q,t=0)=S(q)$ is the static structure factor, which can be determined by static light scattering experiments. It is related to the radial distribution function $g(r)$ by

$$S(q)=1+n\int d^3r\, e^{-i\mathbf{q}\cdot\mathbf{r}}[g(r)-1], \tag{3}$$

with $n=N/\Omega$. The radial distribution function gives the relative conditional probability of finding a particle a distance r apart from another one.

The quantities $S(q,t)$ and $S(q)$ are specified once the particle interactions are known. In colloidal suspensions, one needs to distinguish two types of interparticle interactions: direct (i.e., potential) interactions, which are at the origin of the equilibrium microstructure as quantified by $S(q)$ and $g(r)$, and indirect hydrodynamic interactions. The latter account for the fact that the velocity field, generated in the supporting fluid by the motion of one particle, affects that of the other particles. The suspension dynamics of charged particles, and hence $S(q,t)$, is influenced both by direct (i.e., excluded volume plus electrostatic) and hydrodynamic interactions.

The behavior of $S(q,t)$ depends crucially on the temporal and spatial range probed in the scattering experiments. Typical DLS experiments on colloidal suspensions probe length scales l from $l=2\pi/q\gg\bar{r}$ to $l<\bar{r}$, where $\bar{r}=n^{-1/3}$ is the mean interparticle distance. In the first case, $S(q,t)$ is sensitive to long-wavelength density fluctuations, which are typical of the hydrodynamic regime. In the other limit, $S(q,t)$ is essentially determined by single-particle dynamics, i.e., self-diffusion.

Most of the DLS experiments are confined to correlation times $t>10^{-6}$ s $\gg\tau_B$, where $\tau_B=M/\zeta^0$ is the momentum relaxation time of a spherical colloidal particle of mass M and friction coefficient $\zeta^0=3\pi\eta\sigma$. Here σ is the particle diameter and η is the shear viscosity of the suspending fluid. For typical aqueous suspensions, one finds that $\tau_B\approx10^{-9}-10^{-8}$ s. As a consequence, inertial effects arising from the momentum relaxation of the particles are not resolved, so that only the relaxation of the particle positions is probed. At the shortest resolvable times, $t\approx10^{-6}$ s, the individual particles have diffused only a distance that is a small fraction of their

*Mailing address: Fakultät für Physik, Universität Konstanz, P.O. Box 5560, D-78434 Konstanz, Germany. FAX: +49-7531-883157. Electronic address: gerhard.naegele@uni-konstanz.de

diameters, so that their dynamics is only determined by the single-particle friction and by the hydrodynamic interactions, which can be considered to act instantaneously when $t \gg \tau_B$ [1]. The configurational relaxation of particles, which gives rise to a change of the direct interactions, becomes important at times of the order of the structural relaxation time $\tau_I = \sigma^2/D^0$, where $D^0 = k_B T/\zeta^0$ is the Stokesian free diffusion coefficient. For typical aqueous suspensions, one finds that $\tau_I \approx 10^{-3}$ s such that the short-time regime $\tau_B \ll t \ll \tau_I$ is well separated from the long-time regime $t \gg \tau_I$.

It is known that $S(q,t)$ only decays exponentially for all times $t \gg \tau_B$ and for the experimentally accessible wave numbers q in case of a strongly diluted suspension of noninteracting monodisperse particles. For this limiting case, one finds [1]

$$S^0(q,t) = e^{-q^2 D^0 t}, \qquad (4)$$

where the superscript 0 in $S^0(q,t)$ indicates that both direct and hydrodynamic interactions are vanishingly small. However, significant direct and hydrodynamic forces among the particles give rise to an nonexponential decay of $S(q,t)$, as long as q is not very small. Physically, this is due to the fact that the particles get temporarily trapped in the dynamic cage formed by their next neighbors. The time scale associated with the onset of caging is of the order of the structural relaxation time τ_I.

A phenomenological description of the overall nonexponential relaxation of density fluctuations can be accomplished by using what is known as generalized hydrodynamics [3]. The starting point in a generalized hydrodynamic description is the continuity equation

$$\frac{\partial}{\partial t} \overline{c}(\mathbf{r},t) + \nabla \cdot \overline{\mathbf{j}}(\mathbf{r},t) = 0, \qquad (5)$$

which relates the particle density to the particle current density $\overline{\mathbf{j}}(\mathbf{r},t)$, and it expresses the conservation of the number of particles. The overbar indicates a nonequilibrium average [3]. Close to thermal equilibrium, one can relate the current $\overline{\mathbf{j}}(\mathbf{r},t)$ to the gradients in the particle density by a nonlocal extension of the Fickean law

$$\overline{\mathbf{j}}(\mathbf{r},t) = -\int_0^t dt' \int d^3r' \mathbf{D}_c(|\mathbf{r}-\mathbf{r}'|,t-t') \cdot \nabla' \overline{c}(\mathbf{r}',t'). \qquad (6)$$

This equation states that the averaged current density at position $\mathbf{r}$ and time t arises from gradients of the averaged particle density at neighboring positions $\mathbf{r}'$ and at earlier times $t' \le t$, as mediated by the phenomenological diffusion kernel $\mathbf{D}_c(|\mathbf{r}|,t)$. According to Onsager's regression hypothesis [4], $S(q,t)$ can be expected to obey the same evolution equation as the Fourier component $\overline{c}(\mathbf{q},t)$ of $\overline{c}(\mathbf{r},t)$. Hence, by taking the Fourier-Laplace transform of Eqs. (5) and (6), we find

$$\widetilde{S}(q,z) = \int_0^\infty dt \, e^{-zt} S(q,t) = \frac{S(q)}{z + q^2 \widetilde{D}_c(q,z)}, \qquad (7)$$

where $\widetilde{D}_c(q,z) = \hat{\mathbf{q}} \cdot \widetilde{\mathbf{D}}_c(q,z) \cdot \hat{\mathbf{q}}$ is the longitudinal part of the Fourier-Laplace transform of $\mathbf{D}_c(\mathbf{r},t)$ and $\hat{\mathbf{q}} = \mathbf{q}/q$. The wave vector and frequency (i.e., z) dependence of $\widetilde{\mathbf{D}}_c(q,z)$ will give rise in general to a dynamic structure factor $S(q,t)$ of interacting particles that shows a more complicated dependence on t and q than the simple exponential behavior given by Eq. (4).

There is a limiting regime where Eq. (7) leads to an exponential form for $S(q,t)$. This so-called hydrodynamic regime is characterized by values of $q \ll q_m$ and of $t \gg \tau_I$, with $q^2 t$ kept constant at a value of the order of one. We denote by q_m the position of the principle peak of the static structure factor $S(q)$. Formally this corresponds to the limit $q \to 0$, $z \to 0$ with q^2/z constant. In the hydrodynamic regime, $S(q,t)$ is given by

$$S(q,t) = S(q) e^{-q^2 D_c^L t}, \qquad (8)$$

where $D_c^L = \widetilde{D}_c(q \to 0, z \to 0)$ is denoted as the long-time collective diffusion coefficient. The diffusion coefficient D_c^L can be determined in an alternative way from macroscopic gradient diffusion experiments.

As a phenomenological approach, generalized hydrodynamics provides no methods to predict the diffusion kernel $\widetilde{D}_c(q,z)$. This can only be accomplished on the basis of a microscopic theory that relies on the many-body Smoluchowski equation as the appropriate time evolution equation. Using Mori-Zwanzig projection operator methods, one can derive a memory equation that expresses $S(q,t)$ in terms of a memory function $M_c(q,t)$, the latter being closely related to $\widetilde{D}_c(q,z)$ [3].

In this study we are concerned with the calculation of a reduced memory function $\Delta(q)$ (also termed a nonexponentiality factor), which characterizes the deviation of $S(q,t)$ from a simple exponential in time. The precise definition of $\Delta(q)$ is given in the following section. For calculating $\Delta(q)$, it is necessary to know the time integral of the memory function $M_c(q,t)$. For this purpose, we use a version of the mode-coupling approximation (MCA), as developed recently by Szamel and Löwen [5]. Their MCA scheme is based on earlier work of Cichocki and Hess [6], where it was shown that $M_c(q,t)$ can be further reduced in terms of an irreducible memory function. It is the irreducible memory function to which the MCA scheme of Szamel and Löwen is applied.

Our MCA results for $\Delta(q)$ will be shown to be in good qualitative agreement with all available experimental data, when the theory is extended to account in an approximate way for size polydispersity. Within this extension, it is also necessary to know the time integral of the autocorrelation function $G(q,t)$ of the microscopic one-particle density. We have calculated this time integral in a mode-coupling approximation applied to an irreducible memory function related to $G(q,t)$. It should be pointed out that size polydispersity is present to some extent in almost all colloidal systems. It is quite remarkable that already small amounts of polydispersity can give rise to positive values for the small-q limit of the measurable reduced memory function, in contrast to a vanishing $\Delta(q \to 0)$ found for a genuinely monodisperse suspension.

The direct forces acting between the charged particles are quite sensitive to the amount of residual salt ions dissolved

in the suspension. For this reason, and in order to promote further experimental work, we have also investigated to what extent the nonexponential decay of $S(q,t)$ is influenced by the amount of added electrolyte. We have found that the reduced memory function depends significantly on the ionic strength.

In the following section we outline the Smoluchowski dynamics of collective diffusion, introduce the concept of the reduced memory function, and discuss the general properties of $\Delta(q)$. Section III contains the description of the mode-coupling approximation used together with another simplifying approximation for calculating the reduced memory function of monodisperse systems. The effects of intrinsic size polydispersity are considered in Sec. IV on the basis of what is known as decoupling approximation. Our results, in comparison with experimental and computer simulation data, are presented and discussed in Sec. V. Section VI contains our concluding remarks.

II. SMOLUCHOWSKI DYNAMICS OF COLLECTIVE DIFFUSION

As mentioned in the Introduction, the time and length scales accessible by DLS experiments are restricted to correlation times $t \gg \tau_B$ and corresponding distances $l \gg (D^0 \tau_B)^{1/2}$. This fact allows for a coarse-grained configuration space description based on the generalized Smoluchowski equation (GSE)

$$\frac{\partial}{\partial t} \psi(\mathbf{R}^N, t) = \hat{\Omega}(\mathbf{R}^N) \psi(\mathbf{R}^N, t), \tag{9}$$

where

$$\hat{\Omega}(\mathbf{R}^N) = \sum_{i,j=1}^{N} \frac{\partial}{\partial \mathbf{R}_i} \cdot \mathbf{D}_{ij}(\mathbf{R}^N) \cdot \left[\frac{\partial}{\partial \mathbf{R}_j} - \beta \mathbf{F}_j \right] \tag{10}$$

is the Smoluchowski operator [1–3]. Here $\mathbf{R}^N = \{\mathbf{R}_1, ..., \mathbf{R}^N\}$ denotes the positions of the centers of the spherical particles, the $\mathbf{D}_{ij}(\mathbf{R}^N)$ are diffusivity tensors describing the solvent-mediated hydrodynamic interactions between particles i and j, and $\mathbf{F}_j = -\partial U / \partial \mathbf{R}_j$ denotes the force that all other $(N-1)$ colloidal particles exert on particle j through potential interactions $U(\mathbf{R}^N)$. The GSE is the time evolution equation for the configuration space distribution function $\psi(\mathbf{R}^N, t)$. Using Eq. (1), the dynamic structure factor can be written as

$$S(q,t) = \frac{1}{N} \langle \delta c(\mathbf{q}) e^{\hat{\Omega} t} \delta c(-\mathbf{q}) \rangle, \tag{11}$$

where the angular bracket denotes the canonical ensemble average

$$\langle \ \rangle = \int d\mathbf{R}^N \cdots \psi_{eq}(\mathbf{R}^N). \tag{12}$$

Here $\psi_{eq}(\mathbf{R}^N) = \exp[-\beta U(\mathbf{R}^N)] / \int d\mathbf{R}^N \exp[-\beta U(\mathbf{R}^N)]$ is the equilibrium distribution function. In writing Eq. (11), it is understood that the time evolution operator $\exp \hat{\Omega} t$ acts on everything to its right, including also the equilibrium distribution function.

By employing Mori-Zwanzig projection operator methods, one can derive a memory equation for $S(q,t)$ [7]

$$\frac{\partial}{\partial t} S(q,t) = -q^2 D_{eff}(q) S(q,t) + \int_0^t du \, M_c(q, t-u) \frac{S(q,u)}{S(q)}, \tag{13}$$

which is valid for $t \gg \tau_B$. In Eq. (13)

$$D_{eff}(q) = D^0 \frac{H(q)}{S(q)} \tag{14}$$

is the effective q-dependent short-time collective diffusion coefficient, which is determined by the hydrodynamic function [1,2]

$$H(q) = \frac{1}{ND^0} \sum_{l,j=1}^{N} \langle \hat{\mathbf{q}} \cdot \mathbf{D}_{lj}(\mathbf{R}^N) \cdot \hat{\mathbf{q}} e^{i\mathbf{q} \cdot [\mathbf{R}_l - \mathbf{R}_j]} \rangle \tag{15}$$

and by the static structure factor $S(q)$. The hydrodynamic function $H(q)$ contains the configuration averaged effect of the hydrodynamic interactions on the short-time dynamics. It is a positive definite function, since the $3N \times 3N$ matrix of diffusivity tensors $\mathbf{D}_{lj}(\mathbf{R}^N)$ is also positive definite. For negligibly small hydrodynamic interactions $H(q) = 1$. When hydrodynamic interactions are important, then $H(q)$ becomes q dependent.

The second term in Eq. (13) does not contribute at short times $\tau_B \ll t \ll \tau_I$. Therefore, the short-time expression for $S(q,t)$ is given by

$$S(q,t) = S(q) e^{-q^2 D_{eff}(q) t} \quad (t \ll \tau_I). \tag{16}$$

The effective diffusion coefficient reduces, for small wave numbers $q \ll q_m$, to the short-time collective diffusion $D_c^S = D_{eff}(q \to 0)$, which describes the initial decay of long-wavelength density fluctuations. In systems with strong repulsive forces, and hence low osmotic compressibility (e.g., charge-stabilized suspensions at low ionic strength), D_c^S is found at finite concentrations to be substantially larger than the free particle diffusion coefficient D^0. We further note that $q^2 D_{eff}(q)$ constitutes a contribution to the rate of change of $S(q,t)$ solely determined by the conserved variable $c(q,t)$, whereas the additional rate of change due to all other dynamical variables is contained in the second (memory) term in Eq. (13), where the collective memory function $M_c(q,t)$ appears. The memory term describes the caging effect, and for longer times $(t \gtrsim \tau_I)$ this term will change the time behavior of $S(q,t)$ as compared to its exponential form in Eq. (16).

In the following we discuss general properties of collective diffusion that are related to the form Eq. (13) of the time evolution equation of $S(q,t)$. For this purpose, we do not need to display here explicitly the microscopic expression of $M_c(q,t)$, which is given, e.g., in [1]. By taking the Laplace transform of Eq. (13), and by comparing with the form of $\tilde{S}(q,z)$ given in Eq. (7), it follows

$$\tilde{D}_c(q,z) = D_{eff}(q) - \frac{\tilde{M}_c(q,z)}{q^2 S(q)}, \tag{17}$$

so that the phenomenologically introduced diffusion kernel $\widetilde{D}_c(q,z)$ is now expressed in terms of microscopically defined quantities. As a result, D_c^L can be expressed as

$$D_c^L = D_c^S - \lim_{z \to 0} \lim_{q \to 0} \frac{\widetilde{M}_c(q,z)}{q^2 S(q)}, \qquad (18)$$

with q^2/z kept constant. From Eq. (18) and the mathematical structure of the GSE, one can easily prove the following general ordering relation existing between the long-time and short-time collective diffusion coefficients [8]:

$$0 < D_c^L \leqslant D_c^S. \qquad (19)$$

When only pairwise additive hydrodynamic interactions are important, it can be shown for small q that $\lim_{q \to 0} M_c(q,t)/q^2 = 0$ [9]. In this case we need not distinguish between D_c^L and D_c^S, i.e., $D_c^L = D_c^S = D_c$. Moreover, from Eq. (17) follows then

$$\widetilde{D}_c(q \to 0, z) = D_c = D^0 \frac{H(0)}{S(0)}, \qquad (20)$$

so that in the long-wavelength limit $S(q,t)$ is a single exponential function in time, given by Eq. (16) for $q \to 0$. A proof of this result for many-body hydrodynamic interactions does not exist. The assumption of pairwise additive hydrodynamic interactions is justified for the important case of dilute charge-stabilized suspensions at low ionic strength. In these systems, the particles are kept far apart from each other due to strong electrostatic forces acting among them [10]. As a consequence, only the far-field part of the hydrodynamic interactions contributes to the suspension dynamics and this part is pairwise additive

A suitable measure of the overall nonexponential behavior of $S(q,t)$ is the nonexponentiality factor $\Delta(q)$ defined as [3].

$$\Delta(q) = 1 - \frac{\tau^S(q)}{\bar{\tau}(q)}, \qquad (21)$$

where $\tau^S(q) = [q^2 D_{\text{eff}}(q)]^{-1}$ is the characteristic decay time of the short-time expression Eq. (16) and

$$\bar{\tau}(q) = \int_0^\infty dt \, \frac{S(q,t)}{S(q)} = \frac{\widetilde{S}(q,z=0)}{S(q)} \qquad (22)$$

is the mean relaxation time of $S(q,t)$. The definition (21) of $\Delta(q)$ is such that $\Delta(q) \equiv 0$ if $S(q,t)$ were a simple exponential. The nonexponentiality factor $\Delta(q)$ can be rewritten, using Eqs. (7) and (17), as

$$\Delta(q) = 1 - \frac{\widetilde{D}_c(q,0)}{D_{\text{eff}}(q)} = \frac{\widetilde{M}_c(q,0)}{q^2 D^0 H(q)}, \qquad (23)$$

so that it is essentially determined by the time integral of the collective memory function. For this reason, $\Delta(q)$ is also called reduced memory function. Equation (23) implies that $\Delta(q \to \infty) = 0$.

For noninteracting particles $\tau^S(q) = \bar{\tau}(q) = (q^2 D^0)^{-1}$ and hence $\Delta(q) = 0$, whereas interactions may give rise to an overall slower decay of $S(q,t)$ as compared to its short-time behavior. Therefore it must generally be true that $\bar{\tau}(q) \geqslant \tau^S(q)$ or, equivalently, that

$$0 \leqslant \Delta(q) \leqslant 1. \qquad (24)$$

The ordering relation Eq. (24) can be rewritten with Eq. (23) into the form $0 \leqslant \widetilde{D}_c(q,0) \leqslant D_{\text{eff}}(q)$. A proof of the latter ordering relation has been given by Felderhof and Vogel [11] on the basis of the Smoluchowski dynamics. Notice also that $\widetilde{D}_c(q,z) > 0$ for all $z > 0$. This inequality follows from Eq. (7) and from the fact that any autocorrelation function is monotonically decaying in time when described within the Smoluchowski dynamics [8]. From these properties follow $\widetilde{S}(q,z) > 0$ and $z\widetilde{S}(q,z) < S(q)$, and these inequalities imply that $\widetilde{D}_c(q,z) > 0$.

Because of Eq. (23), $\Delta(q \to 0) = 0$ whenever hydrodynamic interactions can be considered as pairwise additive. However, finite values $\Delta(0) > 0$ are extrapolated from many experimental data on dilute suspensions of highly charged particles. As will be explained in Sec. IV, this experimental observation can be understood by accounting for size polydispersity, which gives rise to an incoherent background of scattered light.

In the following section we describe how $\Delta(q)$ can be computed in mode-coupling approximation. Clearly, any realistic approximation for $\Delta(q)$ must be consistent with Eq. (24).

III. MODE-COUPLING APPROXIMATION

For the calculation of $\Delta(q)$, it is necessary to know the time integral of the collective memory function $M_c(q,t)$. For simplicity, we will neglect hydrodynamic interactions in calculating $\Delta(q)$. This allows us to use a mode-coupling approximation in the form developed by Szamel and Löwen [5], based on earlier work by Cichocki and Hess [6]. The latter authors have shown that $\widetilde{M}_c(q,z)$, or equivalently $\widetilde{D}_c(q,z)$, can be further reduced and expressed in terms of a so-called irreducible collective memory function. Using projection operator techniques, one obtains the expression [3,6]

$$\widetilde{D}_c(q,z) = \frac{k_B T}{S(q)} \frac{1}{\overline{\zeta}_c(q,z)}, \qquad (25)$$

where

$$\widetilde{\zeta}_c(q,z) = \zeta^0 \left[1 + \frac{\Delta \widetilde{\zeta}_c(q,z)}{\zeta^0} \right] \qquad (26)$$

is a generalized friction function. It consists of the bare friction coefficient ζ^0, and a contribution $\Delta \widetilde{\zeta}_c(q,z)$ arising from potential interactions. Note that hydrodynamic interactions are neglected in Eq. (26). Here $\Delta \widetilde{\zeta}_c(q,z)/\zeta^0$ is the Laplace transform of the irreducible collective memory function $\Delta \zeta_c(q,t)/\zeta^0$. This function is related to the memory function $\widetilde{M}_c(q,z)$ in Laplace space by

$$\widetilde{M}_c(q,z) = q^2 D^0 \frac{\Delta \widetilde{\zeta}_c(q,z)/\zeta^0}{1 + \Delta \widetilde{\zeta}_c(q,z)/\zeta^0}. \qquad (27)$$

For this function, Cichocki and Hess have derived the exact result [6]

$$\frac{\Delta\zeta_c(q,t)}{\zeta^0} = q^2\beta^2 D^0 \frac{1}{N}\langle\sigma_\parallel(\mathbf{q})e^{\hat{\Omega}_{\text{irr}}t}\sigma_\parallel(-\mathbf{q})\rangle, \quad (28)$$

where $\sigma_\parallel(\mathbf{q})$ is the microscopic expression for the momentum-averaged longitudinal stress fluctuations, i.e.,

$$\sigma_\parallel(\mathbf{q}) = -\hat{Q}_c\sum_{l=1}^N (i\mathbf{q}\cdot\mathbf{F}_l/q^2 + k_BT)e^{-i\mathbf{q}\cdot\mathbf{r}_l}, \quad (29)$$

and

$$\hat{\Omega}_{\text{irr}}(\mathbf{R}^N) = \hat{Q}_c D^0 \sum_{i=1}^N \frac{\partial}{\partial\mathbf{R}_i}\hat{Q}_i\cdot\left[\frac{\partial}{\partial\mathbf{R}_i} - \beta\mathbf{F}_i\right]\cdot\hat{Q}_c \quad (30)$$

is denoted as the one-particle irreducible Smoluchowski operator. Moreover, $\beta = 1/k_BT$, $\hat{Q}_c = 1 - \hat{P}_c$, and $\hat{P}_c$ is the projection operator

$$\hat{P}_c = \delta c(-\mathbf{q})\rangle\frac{1}{NS(q)}\langle\delta c(\mathbf{q}) \quad (31)$$

on the subspace of density fluctuations. In Eq. (30), there appears a second operator $\hat{Q}_i = 1 - \hat{P}_i$, where $\hat{P}_i$ is defined for $q\neq 0$ as

$$\hat{P}_i = e^{i\mathbf{q}\cdot\mathbf{R}_i}\rangle\langle e^{-i\mathbf{q}\cdot\mathbf{R}_i}. \quad (32)$$

It can be shown that the irreducible memory function $\Delta\zeta_c(q,t)/\zeta^0$ is closely related to the longitudinal component of the generalized dynamic viscosity function [6].

It is interesting to note that Eq. (25) has the form of a Stokes-Einstein relation generalized for interacting particles to wave vector and frequency dependence. Indeed, neglecting interactions gives rise to $S(q) = 1$ and $\widetilde{\zeta}_c(q,z) = \zeta^0$, so that Eq. (25) reduces to $D^0 = k_BT/\zeta^0$.

The nonexponentiality factor can be expressed in terms of the time integral of the irreducible memory function by combining Eqs. (25) and (26) with Eq. (23):

$$\Delta(q) = \frac{\Delta\widetilde{\zeta}_c(q,0)/\zeta^0}{1 + \Delta\widetilde{\zeta}_c(q,0)/\zeta^0}. \quad (33)$$

The MCA is now used to obtain a microscopic expression for $\Delta\zeta_c(q,t)$. We can be rather brief in describing the various steps that lead to the MCA expression for $\Delta\zeta_c(q,t)$, since these have been already discussed in detail by Szamel and Löwen [5], by Wagner [12], and by Kawasaki [13]. The first step of the MCA consists of projecting the longitudinal stress fluctuations $\sigma_\parallel(q)$ in Eq. (28) onto the subspace spanned by bilinear products of density fluctuations. The second step amounts to a factorization approximation for the resulting four-point correlation function and replacing the irreducible operator $\hat{\Omega}_{\text{irr}}$ by the Smoluchowski operator $\hat{\Omega}$. As a result of these two steps, the MCA expression for $\Delta\zeta_c(q,t)$ is obtained

$$\frac{\Delta\zeta_c(q,t)}{\zeta^0} = \frac{\Omega}{2(2\pi)^3}\int d^3k|V(\mathbf{k},\mathbf{q})|^2 S(k,t)S(|\mathbf{q}-\mathbf{k}|,t), \quad (34)$$

where Ω denotes the system volume. In Eq. (34) the irreducible memory function is expressed in terms of the dynamic structure factor and in terms of the static vertex function

$$V(\mathbf{k},\mathbf{q}) = \frac{(D^0)^{1/2}}{N^{3/2}S(k)S(|\mathbf{q}-\mathbf{k}|)}\left\{\frac{q}{S(q)}\langle c(\mathbf{k})c(\mathbf{q}-\mathbf{k})c(-\mathbf{q})\rangle\right.$$
$$\left. -N[\hat{\mathbf{q}}\cdot\mathbf{k}S(|\mathbf{q}-\mathbf{k}|) + \hat{\mathbf{q}}\cdot(\mathbf{q}-\mathbf{k})S(k)]\right\}, \quad (35)$$

which contains both two-point and three-point correlation functions.

We have pointed out above that any realistic approximation for $\Delta(q)$ needs to be consistent with Eq. (24). The given MCA expression for $\Delta\zeta_c(q,t)$ is positive definite and, according to Eqs. (25) and (33), this indeed makes the MCA compatible with Eq. (24) and with the inequality $\widetilde{D}_c(q,z) > 0$ for $z > 0$. Moreover, the MCA applied to the irreducible memory function allows for the possibility of an ideal glass transition in colloidal suspensions [5,14–16].

It should be stressed that the physical compatibility of the MCA might get lost when it is applied to $M_c(q,t)$ instead of the irreducible memory function $\Delta\zeta_c(q,t)/\zeta^0$, as already observed in early applications of the MCA to colloidal fluids [17]. Indeed, Cichocki and Hess [6] and later Kawasaki [13] have clearly demonstrated that approximations such as the MCA are performed in a safer way for the irreducible memory function than for $M_c(q,t)$.

We focus now on the three-point correlation function in Eq. (35), which can be expressed in the form

$$\langle c(\mathbf{k})c(\mathbf{q}-\mathbf{k})c(-\mathbf{q})\rangle = N[-2 + S(q) + S(k) + S(|\mathbf{q}-\mathbf{k}|)$$
$$+ n^2\hat{g}^{(3)}(\mathbf{k},\mathbf{q}-\mathbf{k})], \quad (36)$$

where $\hat{g}^{(3)}(\mathbf{k},\mathbf{k}')$ is the Fourier transform of the static triplet correlation function $g^{(3)}(\mathbf{r},\mathbf{r}')$ [18], i.e.,

$$\hat{g}^{(3)}(\mathbf{k},\mathbf{k}') = \int d^3r\int d^3r' e^{-i\mathbf{k}\cdot\mathbf{r}}e^{-i\mathbf{k}'\cdot\mathbf{r}'}g^{(3)}(\mathbf{r},\mathbf{r}'). \quad (37)$$

Three-body correlations are difficult to calculate and require additional approximations. Following Szamel and Löwen [5], we employ as a third approximation the so-called convolution approximation in Fourier space [19]

$$\langle c(\mathbf{k})c(\mathbf{q}-\mathbf{k})c(-\mathbf{q})\rangle = NS(k)S(|\mathbf{q}-\mathbf{k}|)S(q). \quad (38)$$

Substitution of Eq. (38) into Eq. (35) leads to the expression

$$V(\mathbf{k},\mathbf{q}) = \left(\frac{nD^0}{\Omega}\right)^{1/2}[\hat{\mathbf{q}}\cdot\mathbf{k}c(k) + \hat{\mathbf{q}}\cdot(\mathbf{q}-\mathbf{k})c(|\mathbf{q}-\mathbf{k}|)] \quad (39)$$

for the vertex function. Here $nc(k) = 1 - S^{-1}(k)$ and $c(k)$ is the Fourier transform of the Ornstein-Zernike direct correlation function. This quantity should not be confused with the microscopic density $c(\mathbf{q})$. The form of the vertex function in

Eq. (39) has been successfully used in the study of the glass transition in simple fluids and of colloidal suspensions [5,13–16].

The MCA becomes exact in the weak coupling limit. In this limit, the particles are assumed to interact by a weak and continuous pair potential $u(r)$, with $\beta u(r) \ll 1$. Ackerson [7] has derived the exact weak coupling expression for the memory function $M_c(q,t)$. It is easily seen that the weak coupling limit is recovered from Eqs. (34) and (39) by noting that $M_c(q,t) = q^2 D^0 \Delta \zeta_c(q,t)/\zeta^0 + O(u^4)$, $c(q)$ reduces to $-\beta u(q)$ to first order in u, and $S(q,t) = \exp(-q^2 D^0 t)$ to zeroth order in u.

Equations (39), (34), (25), and (7) form a closed set of equations from which $S(q,t)$ could, in principle, be calculated self-consistently with the static structure factor $S(q)$ as input. However, a full self-consistent calculation would be very tedious, particularly since one part of the equations is expressed in the time domain and the other part in the space of Laplace transforms.

Instead of solving this complicated nonlinear problem, we rather consider a simplified version, which amounts to replacing the dynamic structure factor under the integral in Eq. (34) by its short-time expression, i.e., by $S(q,t) = S(q)\exp[-q^2 D^0 t/S(q)]$. This allows one to perform the angular integration to obtain

$$
\frac{\Delta \zeta_c(q,t)}{\zeta^0} = \frac{nD^0}{2(2\pi)^2} \int_0^\infty dk \ k^2 \int_{-1}^1 d\mu [\mu k c(k)
$$
$$
+ (q-\mu k)c(k')]^2 S(k)S(k')
$$
$$
\times \exp\left[-D^0 t\left(\frac{k^2}{S(k)} + \frac{k'^2}{S(k')} \right) \right], \qquad (40)
$$

where $k' = |\mathbf{q} - \mathbf{k}| = \sqrt{q^2 + k^2 - 2qk\mu}$ and $\mu = \hat{\mathbf{q}} \cdot \hat{\mathbf{k}}$. The time integral of this expression gives

$$
\frac{\Delta \tilde{\zeta}_c(q,0)}{\zeta^0} = \frac{n}{2(2\pi)^2} \int_0^\infty dk \ k^2 S(k) \int_{-1}^1 d\mu [\mu k c(k)
$$
$$
+ (q-\mu k)c(k')]^2 \frac{S(k')}{k^2/S(k) + k'^2/S(k')}. \qquad (41)
$$

The function $\Delta(q)$ is then calculated using Eq. (33). Therefore, $\Delta(q)$ is solely expressed in terms of the static structure of the suspension.

A related procedure to determine $\Delta(q)$ has been used by Hess and Klein [3], who based their calculation on the Fokker-Planck equation in the overdamped limit and made use of a somewhat different mode-coupling ansatz for $\Delta \zeta_c(q,t)$, which gives rise to a vertex function $V(\mathbf{k},\mathbf{q})$ different from the one in Eq. (39) (cf. also [12]). Their result for $\Delta(q)$ has been compared to experiments, but particularly for small q no good agreement was found. This finding raised some doubts on the validity of the MCA [20].

We will show that the version of MCA based on the vertex function in Eq. (39) gives results for $\Delta(q)$, which compare favorably with available experimental data. The comparison is particularly good for small q when polydispersity effects are taken into account. The experimental data seem to extrapolate in general to a finite value of $\Delta(q)$ as $q \to 0$ [20–22], whereas theory predicts that $\Delta(q) = O(q^2)$ for $q \to 0$ as long as the suspension is genuinely monodisperse. We will show in the following that even small amounts of polydispersity can give rise to a finite value of the (measurable) nonexponentiality factor.

IV. POLYDISPERSITY EFFECTS

A polydisperse suspension can be described as an m-component mixture. In DLS experiments, a measurable dynamic structure factor is determined, which reads [1,2,8]

$$
S_M(q,t) = \frac{1}{\overline{f^2}(q)} \sum_{\alpha,\beta=1}^m (x_\alpha x_\beta)^{1/2} f_\alpha(q) f_\beta(q) S_{\alpha\beta}(q,t). \tag{42}
$$

Here $S_{\alpha\beta}(q,t)$ is the correlation function of density fluctuations of components α and β, and $f_\alpha(q)$ is the scattering amplitude of particles of component α, described by

$$
f_\alpha(q) = \Delta \nu_p \sigma_\alpha^3 b(q\sigma_\alpha/2). \tag{43}
$$

In this expression, $\Delta \nu_p$ is the particle refractive index relative to the solvent and σ_α and $x_\alpha = N_\alpha/N$ are, respectively, the particle diameter and molar fraction of component α. The form amplitude $b(q\sigma_\alpha/2)$ of an α-type homogeneous spherical particle is given by $b(x) = 3j_1(x)/x$, where $j_1(x)$ is the spherical Bessel function of first order.

In the following we will restrict our analysis to the important case where the distribution of the particle diameters is rather narrowly peaked around a mean diameter $\bar{\sigma}$. Then, it is possible to neglect the effects of polydispersity on the correlation functions $S_{\alpha\beta}(q,t)$ and to consider only the size related scattering polydispersity described by the $f_\alpha(q)$. With this assumption the measurable dynamic structure factor reduces to what is known as decoupling approximation [1,2,8,23]

$$
S_M(q,t) \approx S_D(q,t) = [1 - X(q)]S(q,t) + X(q)G(q,t), \tag{44}
$$

where

$$
X(q) = 1 - \frac{\overline{f}(q)^2}{\overline{f^2}(q)} \approx 9s^2 \tag{45}
$$

and $s = (\langle \sigma^2 \rangle - \bar{\sigma}^2)^{1/2}/\bar{\sigma}$ is the relative standard deviation of the distribution of particle diameters. Furthermore,

$$
\overline{f^n}(q) = \sum_{\alpha=1}^m x_\alpha f_\alpha^n(q) \tag{46}
$$

is the nth moment of the distribution of scattering amplitudes. The function $X(q)$ is bounded according to $0 \leq X(q) \leq 1$ and, for small s, is well approximated by $9s^2$ as expressed in Eq. (45).

The self-intermediate scattering function $G(q,t)$, appearing in Eq. (44), is the autocorrelation function of the microscopic one-particle density, i.e.,

$$
G(q,t) = \langle e^{i\mathbf{q} \cdot [\mathbf{R}_1(t) - \mathbf{R}_1(0)]} \rangle, \tag{47}
$$

where the index 1 refers to a representative particle. Both $S(q,t)$ and $G(q,t)$ on the right-hand side of Eq. (44) correspond to the effective monodisperse system for which all particles are of the same diameter $\bar{\sigma}$ [1,2,8]. The first term on the right-hand side of (44) is due to interparticle correlations and will therefore be addressed as the coherent part. The second term in (44) proportional to $G(q,t)$ arises from single particle diffusion and leads to an incoherent scattering contribution. Hence we refer to it as the incoherent part. We will show in the following that the incoherent part strongly influences the nonexponential decay of the dynamic scattering function particularly when q is small.

It is now crucial to realize that it is the nonexponentiality factor $\Delta_D(q)$ of $S_M(q,t) \approx S_D(q,t)$, and not $\Delta(q)$, that is determined in conventional DLS experiments. Similar to Eq. (21), $\Delta_D(q)$ is defined as

$$\Delta_D(q) = 1 - \frac{\tau_D^S(q)}{\bar{\tau}_D(q)}, \quad (48)$$

where $\tau_D^S(q) = S_D(q)/(q^2 D^0)$ is the relaxation time of $S_D(q,t)$ at short times, as obtained from a first cumulant analysis of $S_D(q,t)$. This should be contrasted with the relaxation time $\tau^S(q) = S(q)/(q^2 D^0)$ for the monodisperse case. The ratio of the two relaxation times is

$$\frac{\tau_D^S(q)}{\tau^S(q)} = \frac{S_D(q)}{S(q)} \approx 1 + 9s^2 \left(\frac{1}{S(q)} - 1 \right), \quad (49)$$

showing that the initial relaxation of $S_D(q,t)$ is faster than that of $S(q,t)$ for those values q for which $S(q) < 1$.

The expression found for $\tau_D^S(q)$ is also due to the short-time expression for $G(q,t)$, which is given by $\exp(-D_s^S q^2 t)$. Here D_s^S is the short-time self-diffusion coefficient, which is equal to the free diffusion coefficient D^0 when hydrodynamic interactions are neglected. The mean relaxation of $S_D(q,t)$ is characterized, in analogy to Eq. (22), by

$$\bar{\tau}_D(q) = \int_0^\infty dt \, \frac{S_D(q,t)}{S_D(q)} = \frac{\tilde{S}_D(q,0)}{S_D(q)}, \quad (50)$$

with

$$\tilde{S}_D(q,0) = [1 - X(q)]\tilde{S}(q,0) + X(q)\tilde{G}(q,0). \quad (51)$$

It can easily be seen from Eq. (44) that polydispersity will alter the previous results for the nonexponentiality factor, in particular at small values of q. For $q \ll q_m$, $G(q,t) = \exp[-q^2 W(t)]$ and $S_D(q,t)$ can then be written in the form

$$S_D(q,t) \approx (1 - 9s^2)S(0)\exp\left[-q^2 \frac{D^0}{S(0)} t \right]$$
$$+ 9s^2 \exp[-q^2 W(t)], \quad (52)$$

where $s \ll 1$ and

$$W(t) = \tfrac{1}{6}\langle [\mathbf{R}_1(t) - \mathbf{R}_1(0)]^2 \rangle \quad (53)$$

denotes the particle mean square displacement. The limiting behavior of $W(t)$ is $W(t) \approx D_s^S t$ for $\tau_B \ll t \ll \tau_I$ and

$W(t) \approx D_s^L t$ for $t \gg \tau_I$, where $D_s^L t$ denotes the long-time self-diffusion coefficient. It can be shown that $D_s^S > D_s^L$ [8], which is due to the hindrance of the Brownian motion of a particle by its direct and hydrodynamic interactions with neighboring particles. The relative osmotic compressibility $S(0)$ of a strongly correlated system is very small (of order 10^{-2}). Therefore, the more slowly decaying second term in Eq. (52), which represents the incoherent scattering contribution [1,2], is particularly important and gives rise to values $\Delta_D(0) > 0$, as suggested by the experiment.

The time integral of $S(q,t)$ can be expressed in terms of $\Delta(q)$ using Eqs. (7) and (23) as

$$\tilde{S}(q,0) = \frac{S^2(q)}{q^2 D^0[1 - \Delta(q)]}. \quad (54)$$

Since from Eqs. (48) and (50)

$$\Delta_D(q) = 1 - \frac{S_D^2(q)}{q^2 D^0 \tilde{S}_D(q,0)}, \quad (55)$$

the only quantity needed besides $\Delta(q)$ to calculate the measurable nonexponentiality factor $\Delta_D(q)$ is the time integral $\tilde{G}(q,0)$ of the self-intermediate scattering function. It is obtained by a projection operator method, similar to the one used for the collective case. We only outline here the major steps. First, the Laplace transform of $G(q,t)$ is expressed, similar to Eq. (7), in terms of a generalized wave-number- and frequency-dependent self-diffusion function $\tilde{D}_s(q,z)$ according to [3]

$$\tilde{G}(q,z) = \frac{1}{z + q^2 \tilde{D}_s(q,z)}. \quad (56)$$

From the general properties of the Smoluchowski equation it follows that $\tilde{D}_s(q,z)$ is positive definite for $z > 0$. The self-diffusion function $\tilde{D}_s(q,z)$ is related to the longitudinal part of the generalized self-friction function $\zeta^0 + \Delta\tilde{\zeta}_s(q,z)$ by

$$\tilde{D}_s(q,z) = \frac{k_B T}{\zeta^0 + \Delta\tilde{\zeta}_s(q,z)}, \quad (57)$$

where the nontrivial part $\Delta\tilde{\zeta}_s(q,z)$ arises from the potential interactions (hydrodynamic interactions are neglected in this work).

The hydrodynamic limit of the generalized diffusion function is equal to the long-time self-diffusion coefficient, i.e., $D_s^L = \lim_{z \to 0} \lim_{q \to 0} \tilde{D}_s(q,z)$, and with Eq. (57) follows

$$D^* = \left[1 + \frac{\Delta\tilde{\zeta}_s(0,0)}{\zeta^0} \right]^{-1}, \quad (58)$$

where $D^* = D_s^L/D^0$ denotes the normalized long-time self-diffusion coefficient. We are now in the position to show explicitly that $\Delta_D(0) \neq 0$. To this end, we combine the relation

$$q^2 D^0 \tilde{G}(q,0) = 1 + \frac{\Delta\tilde{\zeta}_s(q,0)}{\zeta^0} \quad (59)$$

with Eq. (55). By observing Eq. (58) and noting that $\Delta(0)=0$, the following result is obtained:

$$\Delta_D(0)=1-\frac{S_D^2(0)}{[1-X(0)]S^2(0)+X(0)/D^*},\qquad(60)$$

which relates $\Delta_D(0)$ to D^* and to static quantities. From this expression the measurable nonexponentiality factor is seen to be nonvanishing provided that $s>0$.

To obtain $\Delta_D(q)$, we need to know the normalized self-friction function $\Delta\zeta_s(q,t)/\zeta^0$, which is the one-particle irreducible memory function in case of self-diffusion. To be consistent with our earlier treatment of $\Delta\zeta_c(q,t)/\zeta^0$, this function will also be evaluated in the MCA. We will employ the following (positive definite) MCA expression, which was derived by Hess and Klein [3] (cf. also [17,24]):

$$\frac{\Delta\zeta_s(q,t)}{\zeta^0}=\frac{nD^0}{(2\pi)^3}\int d^3k(\hat{\mathbf{q}}\cdot\mathbf{k})^2c^2(k)G(|\mathbf{q}-\mathbf{k}|,t)S(k,t).$$
$$(61)$$

The MCA expression given here relates the irreducible memory function to a convolution-type integral over the self- and collective correlation functions $G(q,t)$ and $S(q,t)$, weighted by a static vertex function proportional to the square of the direct correlation function. Similar to the collective case, the MCA expression for $\Delta\zeta_s(q,t)/\zeta^0$ becomes exact in the weak coupling limit.

A closed set of equations for $S(q,t)$ and $G(q,t)$ is given by combining Eqs. (7), (25), (34), and (39) describing collective diffusion with the corresponding Eqs. (56), (57), and (61) for self-diffusion. Instead of attempting this fully self-consistent calculation, we have calculated $\Delta(q)$ as explained in Sec. III [cf. Eqs. (33) and (41)]. The integral on the right-hand side of Eq. (61) is approximated by substituting $S(q,t)$ once again by its short-time expression, whereas $G(q,t)$ is replaced by its limiting hydrodynamic form $\exp(-q^2D^0D^*t)$. One can now perform the time integral and the angular integrations to obtain

$$\frac{\Delta\widetilde{\zeta}_s(q,0)}{\zeta^0}=\frac{n}{(2\pi)^2}\int_0^\infty dk[k^2c(k)]^2S(k)$$

$$\times\int_{-1}^1 d\mu\,\frac{\mu^2}{k^2/S(k)+k'^2D^*},\qquad(62)$$

where $k'=(q^2+k^2-2qk\mu)^{1/2}$. Substitution of Eq. (62) into Eq. (58) gives the self-consistent equation

$$D^*=\left[1+\frac{1}{6\pi^2n}\int_0^\infty dk\,k^2\,\frac{[S(k)-1]^2}{1+D^*S(k)}\right]^{-1},\qquad(63)$$

which can be solved iteratively for the unique solution D^* [25]. This completes our calculation of the nonexponentiality factor $\Delta_D(q)$ for a polydisperse suspension in decoupling approximation. The only input needed is the static structure factor $S(q)$ or, equivalently, the direct correlation function $c(q)$.
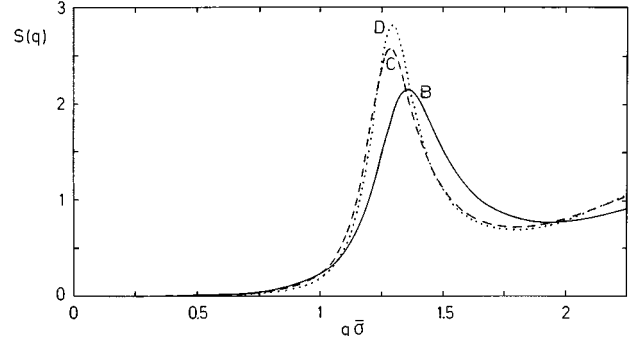

FIG. 1. RMSA results of the static structure factor $S(q)$ for samples B (solid line), C (dashed line), and D (dotted line). The wave number q is scaled by the mean particle diameter $\bar{\sigma}$. The system parameters are taken from the experimental work of Taylor and Ackerson [20] and are summarized in Table I.

V. RESULTS AND DISCUSSION

Our theoretical results for the nonexponential relaxation of density fluctuations have been applied to strongly correlated charge-stabilized suspensions, which have been investigated recently using DLS. These systems can be conveniently described by the effective macroion fluid model. In this model, the effective pair potential $u(r)$ between two particles consists of a hard core diameter σ and a screened Coulomb potential

$$\beta u(r)=K\sigma\frac{e^{-\kappa(r-\sigma)}}{r}\qquad(64)$$

for $r>\sigma$. The dimensionless coupling constant K is given, within the Derjaguin-Landau-Verwey-Overbeek theory, by [26]

$$K=\frac{L_B}{\sigma}\left(\frac{Z}{1+\kappa\sigma/2}\right)^2,\qquad(65)$$

with $L_B=e^2/\epsilon k_BT$ being the Bjerrum length, e the elementary charge, and ϵ the dielectric constant of the suspending solvent. The effective charge (in units of e) of a colloidal particle is denoted by Z. The equation

$$\kappa^2=4\pi L_B[n|Z|+2n_s]\qquad(66)$$

defines the Debye-Hückel screening parameter κ, where n_s is the number density of an added 1-1 electrolyte and the counterions are assumed to be monovalent.

The only input needed to calculate $\Delta(q)$ and $\Delta_D(q)$ is the static structure factor $S(q)$. We have calculated $S(q)$ from the pair potential Eq. (64) by using the rescaled mean spherical approximation (RMSA). This integral equation method has been found to be an efficient fitting device of experimentally determined structure factors [8,27]. The parameters in Eqs. (64)–(66) are chosen to correspond to several experiments that have been performed to determine the nonexponentiality factor. The effective charge Z used in our calculations is determined from fitting the peak height of the calculated $S(q)$ to the experimentally determined one. This fitting procedure leads to an optimized static input.

Figure 1 shows the RMSA fit results of $S(q)$ for three

TABLE I. Parameters characterizing a selection of charge-stabilized suspensions of spherical particles investigated, respectively, by Taylor and Ackerson [20], Härt et al. [22], and Müller [21]. For clarity, these samples are denoted as in the original references. Particle diameter, σ; number density, n; volume fraction, $\Phi = \pi n \sigma^3 / 6$; total screening parameter, κ; coupling factor, K; effective valency, Z; effective surface potential, $\psi_0 = [4K/(\beta \epsilon \sigma)]^{1/2}$.

| Parameters | Taylor and Ackerson | | | | Müller | | |
	B	C	D	Härtl et al.	ST	WX	YZ
σ (nm)	109	109	109	80	100	100	100
$n \times 10^{-9}$ nm^{-3}	6.0	5.2	5.3	1.95	2.2	2.4	2.5
$\Phi \times 10^{-3}$	4.1	3.5	3.6	0.52	1.15	1.28	1.3
$\kappa \sigma$	0.574	0.248	0.173	0.22	0.9	0.7	0.28
K	500	619	741	1002	358	860	708
Z	360	350	370	373	329	475	364
ψ_0 (mV)	92	103	113	151	82	127	115
$q_m \sigma$	1.36	1.30	1.30	0.69	1.05	0.96	0.93

aqueous suspensions of charged latex spheres investigated by Taylor and Ackerson [20]. The system parameters characterizing these samples are listed in Table I. Samples $B-D$ have been treated by ion exchange resins, so that essentially all excess ions have been removed. This gives rise to very low osmotic compressibility, i.e., very low values of $S(q=0)$ as shown in Fig. 1.

Another careful study of the relaxation of the dynamic structure factor was done very recently by Müller [21]. In Fig. 2 we display the RMSA fit results of $S(q)$ for his samples (id83)ST, (id83)WX, and (id83)YZ, calculated for system parameters as quoted in Table I. There are residual salt ions left in samples ST and WX, leading to less pronounced variations of $S(q)$ and an enhanced osmotic compressibility.

Similar experiments have been performed by Härtl et al. [22] on dilute suspensions of polymer colloid particles. These authors estimated the polydispersity (i.e., relative standard deviation) as $s=0.062$. A comparison between $S(q)$, corresponding to $s=0$, and the measurable static structure factor $S_D(q)$ evaluated in decoupling approximation (for $s=0.062$) is presented in Fig. 3. Also shown in this figure is the form factor $P(q)=b(q\sigma/2)^2$, with $b(x)$ as defined following Eq. (43). Both $S(q)$ and $S_D(q)$ are obtained using the RMSA, with the RMSA $S(q)$ being fitted to the experimen-

tally determined structure factor. It is interesting to note that $S_D(q)$ is nearly identical to $S(q)$. The only differences between the two functions are observed at $q=q_m$ and, most significantly, at $q \approx 0$, where $S_D(q)$ becomes larger than $S(q)$.

We proceed now to discuss our theoretical results for $\Delta(q)$ and $\Delta_D(q)$ in comparison with the experimental findings. Figure 4 shows our MCA results for the deionized samples $B-D$ investigated by Taylor and Ackerson [20]. The graphs going to zero with $O(q^2)$ for $q \to 0$ correspond to treating these systems as ideally monodisperse, whereas the other three graphs are obtained by assuming a polydispersity of $s=0.05$. The predictions of the mode-coupling theory used in this work are that both $\Delta(q)$ and $\Delta_D(q)$ have a local minimum (maximum) near $q=q_m$ ($q=1.5q_m$) and both are declining with increasing q for $q>1.5q_m$. Most importantly, very small amounts of size polydispersity can give rise to a dramatic difference between $\Delta(q)$ and $\Delta_D(q)$ for $q<q_m$. This difference can qualitatively be understood by extending the reasoning given in Sec. IV following Eq. (53): since $S(q) \ll 1$ for $q \ll q_m$ (in deionized suspensions), it follows that
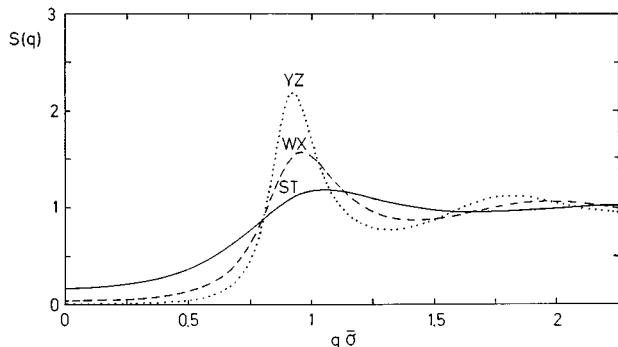
FIG. 2. RMSA results of $S(q)$ for samples id83ST (solid line), id83WX (dashed line), and id83YZ (dotted line). The system parameters are taken from Müller [21] and are listed in Table I.
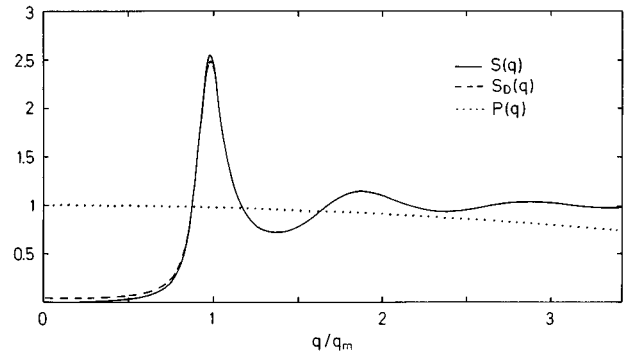
FIG. 3. Comparison between the static structure factor $S(q)$, corresponding to vanishing polydispersity, and the measurable static structure factor $S_D(q)$ evaluated in decoupling approximation for relative standard deviation $s=0.062$. Both $S(q)$ and $S_D(q)$ are calculated using the RMSA and are plotted versus q scaled by the position q_m of the principal peak of $S(q)$. System parameters are taken from Härtl et al. [22] and are listed in Table I. The dotted line shows the form factor $P(q)$.
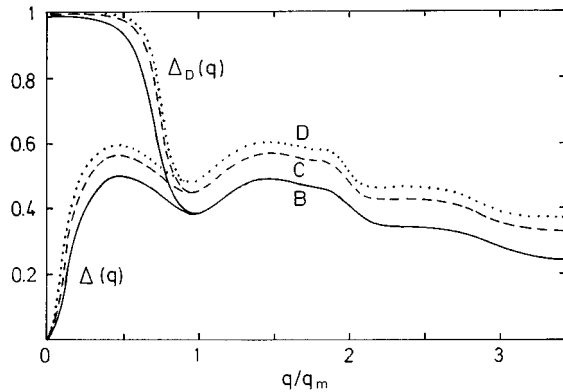
FIG. 4. Comparison between the MCA results for nonexponentiality factors $\Delta(q)$ and $\Delta_D(q)$ versus q/q_m for $s=0$ and 0.05, respectively. The results shown in this figure correspond to samples B (solid line), C (dashed line), and D (dotted line) of Taylor and Ackerson [20]. Note that already a small amount of polydispersity gives rise to $\Delta_D(q\rightarrow 0)>0$. The corresponding RMSA of the $S(q)$ of Fig. 1 are used as static input.

the measurable structure factor is essentially determined in this regime by the second term of Eq. (52). Furthermore, the decay rate of $S(q,t)$ is for small q approximately given by $q^2D^0/S(q)$, whereas the small-q decay rate of $G(q,t)$ is $q^2\dot{W}(t)$, which is much smaller. The slow decay of $G(q,t)$ gives rise to a comparatively large value of $\overline{\tau}_D(q)$, such that according to Eq. (48), $\Delta_D(q\ll q_m)$ attains a value close to one. In short, the decay of $S_D(q,t)$ at $q\ll q_m$ is dominated by self-diffusion.

On the other hand, for $q\gtrsim q_m$, it is the first term (i.e., the coherent contribution) in Eq. (44) that essentially determines $S_D(q,t)$, and this finding originates from $X(q)\propto 9s^2\ll 1$, from $S(q\gtrsim q_m)=O(1)$, and from the fact that the decay rate of $S(q,t)$ is now of the same order as the one of $G(q,t)$. This explains why $\Delta_D(q)$ is practically equal to $\Delta(q)$ when $q>q_m$.

In Fig. 5 the experimental results for $\Delta_D(q)$ of Taylor and Ackerson are compared to the calculated ones. The qualitative predictions of the MCA noted above are nicely confirmed by the experiment and the agreement is particularly
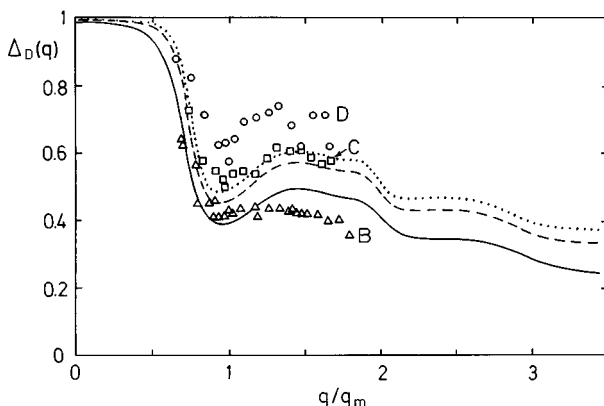

FIG. 5. Experimental results for the measurable nonexponentiality factor of samples B ($\triangle$), C ($\square$), and D ($\bigcirc$) taken from Taylor and Ackerson [20]. For comparison, the corresponding MCA results for $\Delta_D(q)$ are included, by assuming that $s=0.05$.
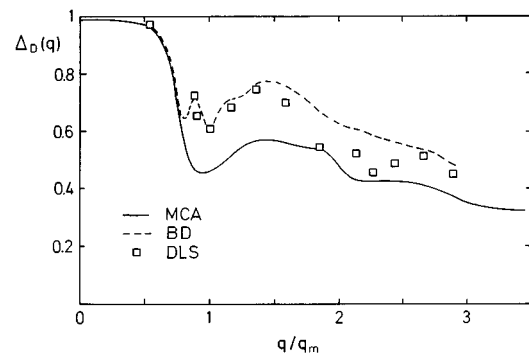

FIG. 6. Measurable nonexponentiality factor $\Delta_D(q)$ for an aqueous suspension of polymer colloid spheres studied by Härtl et al. [22]. The symbols $\square$ denote dynamic light scattering data, taken from [22]. Solid line, MCA result with static input $S_D(q)$ as shown in Fig. 3. Dashed line, Brownian dynamics result for $\Delta_D(q)$, taken from [22]. The same value $s=0.062$ has been used in both the MCA calculation and in the simulation.

good at small q, where polydispersity becomes most important. We notice further that both experiment and theory show the expected increase of $\Delta_D(q)$ with increasing particle correlations. At larger q, the MCA has the tendency to underestimate somewhat the amount of nonexponentiality created by the particle interaction, with the exception of sample B (cf. also Figs. 6 and 7).

Figure 6 displays the calculated $\Delta_D(q)$ in comparison with the corresponding DLS result of Härtl et al. [22]. The authors also performed Brownian dynamics (BD) simulations to determine $\Delta(q)$ and $\Delta_D(q)$ and found a difference between the two for $q<q_m$ in accordance with the present findings. In the simulations, hydrodynamic interaction is not considered and $\Delta_D(q)$ is calculated also on the basis of the decoupling approximation for $S_M(q,t)$. The figure illustrates again the tendency of the MCA to somewhat underestimate the degree of nonexponentiality. The work of Härtl et al. includes, to the best of our knowledge, the only BD data published so far for the nonexponentiality factor. This is not surprising since BD simulations of collective properties are very demanding and time consuming when carried over extensive ranges of times and wave numbers. Therefore, there is a need for approximations such as the MCA, which give at least a qualitatively correct description of $\Delta_D(q)$.

The experimental results of Müller [21] are shown in Fig. 7 together with the MCA determination of $\Delta_D(q)$. In calculating $\Delta_D(q)$ for this figure, we used the input $S(q)$ of Fig. 2. We find the results of Müller to be well reproduced by our calculations. For sample (id83)ST, $\Delta_D(0)$ is significantly smaller than one; this system is weakly correlated due to the presence of residual salt ions, i.e., it has only a weak structure in $S(q)$ (cf. Fig. 2 and the value for $\kappa\sigma$ given in Table I).

In all three sets of experiments the limit $q\rightarrow 0$ of $\Delta_D(q)$ was not achieved, although all results seem to indicate that $\Delta_D(q\rightarrow 0)$ is indeed finite. To illustrate this point, we have calculated $\Delta_D(q=0)$ as a function of the polydispersity index s for the system parameters corresponding to Figs. 7 and 2. The results are shown in Fig. 8. They clearly show that in strongly correlated (e.g., deionized) suspensions already very small amounts of polydispersity give rise to a finite value of
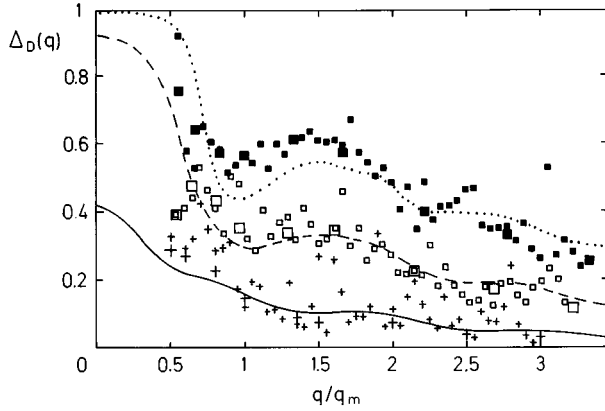
FIG. 7. Experimental results for the nonexponentiality factor of samples id83ST (+), id83WX (□), and id83YZ (■) as given by Müller [21]. Large symbols, data obtained from averaged relaxation spectra including long-time dynamic light scattering; small symbols, data obtained from temporal integration of the dynamic structure factor. The MCA results for samples id83ST (solid line), id83WX (dashed line), and id83YZ (dotted line) have been calculated using $s=0.05$.

the measurable nonexponentiality factor at $q=0$. It will therefore be very difficult, if not impossible, to show experimentally whether the small-q limit of the dynamic structure factor of a one-component system is a single exponential of time for all t, which is predicted for truly monodisperse particles when hydrodynamic interactions are assumed to be pairwise additive. Obviously, $\Delta_D(q)$ reduces to $\Delta(q)$ for $s \rightarrow 0$. From Eq. (60), we find that $\Delta_D(0) \approx 9s^2/[D^*S^2(0)]$, provided that $S(0)$ is small compared to one and that $s^2 \ll S(0)$. For comparison, our RMSA calculations give $S(0) \approx 0.165$ for sample ST and $S(0) \approx 0.003$ for the most strongly correlated sample YZ.

The calculations of $\Delta_D(q)$ shown in this work are based on the decoupling approximation $S_D(q,t)$ for $S_M(q,t)$. This approximation predicts a vanishing nonexponentiality factor $\Delta_D^0(q)$ in case of a size polydisperse system of noninteracting particles. While this is not exact, we will now show by an exact calculation that $\Delta_M^0(q) \approx 0$ as long as $s < 0.1$. Here $\Delta_M^0(q)$ denotes the measurable nonexponentiality factor of
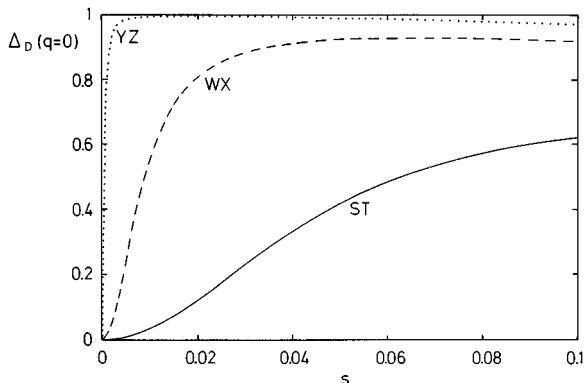

FIG. 8. MCA results for $\Delta_D(q=0)$ as a function of the relative standard deviation s for samples id83ST (solid line), id83WX (dashed line), and id83YZ (dotted line).
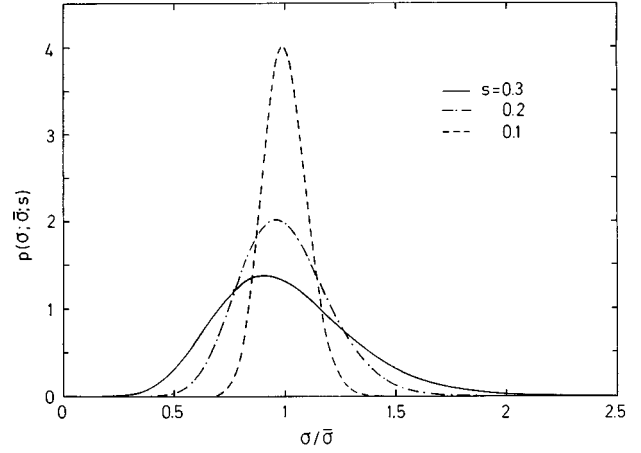

FIG. 9. Continuous Schulz distribution $p(\sigma;\bar{\sigma};s)$ of particle sizes for values of the relative standard deviation s, as indicated in the figure.

an interaction-free system (indicated by the superscript 0), which is defined as

$$\Delta_M^0(q) = 1 - \frac{\tau_M^{0,S}(q)}{\bar{\tau}_M^0(q)}, \qquad (67)$$

with

$$\tau_M^{0,S}(q) = -[\dot{S}_M^0(q,t=0)]^{-1} \qquad (68)$$

and

$$\bar{\tau}_M^0(q) = \int_0^\infty dt\, S_M^0(q,t). \qquad (69)$$

The dynamic structure factor of a size polydisperse system of noninteracting and uniform particles reads [1]

$$S_M^0(q,t) = \frac{1}{\overline{b^2}(q\sigma/2)} \int_0^\infty d\sigma\, p(\sigma)[\sigma^3 b(q\sigma/2)]^2 e^{-q^2 D^0(\sigma)t}, \qquad (70)$$

with $D^0(\sigma) = k_B T/(3\pi\eta\sigma)$ and

$$\overline{b^2}(q\sigma/2) = \int_0^\infty d\sigma\, p(\sigma)[\sigma^3 b(q\sigma/2)]^2. \qquad (71)$$

In Eqs. (70) and (71), $p(\sigma)$ denotes the distribution of particle diameters. For $p(\sigma)$, we chose the two-parametric Schulz distribution $p(\sigma;\bar{\sigma};s)$, characterized by the mean diameter $\bar{\sigma}$ and the polydispersity index s [8,28]. This distribution function allows for good fits of the experimentally determined size distribution in many sorts of colloidal suspensions [8,28]. While other choices exist for the size distribution function, the detailed shape of this distribution is not crucial for sufficiently small s. Figure 9 shows the graphs of $p(\sigma;\bar{\sigma};s)$ for three values of s as indicated in the figure. The corresponding results for $S_M^0(q,t)$, plotted versus $q^2 D^0(\bar{\sigma})t$, are given in Fig. 10. Large size polydispersity gives rise to a slower decay of $S_M^0(q,t)$. We note further that there is only a minor change in the decay of $S_M^0(q,t)$ as long as s is
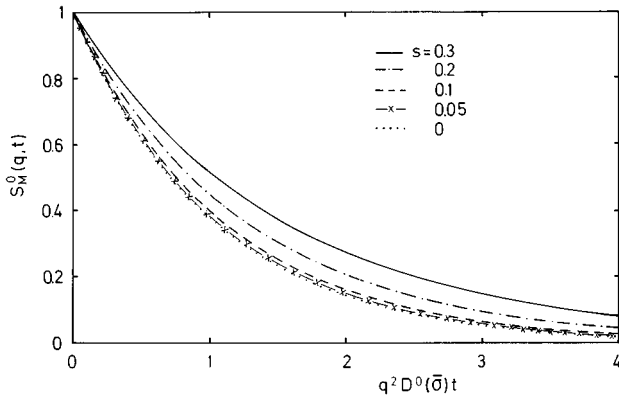
FIG. 10. Measurable dynamic structure factor $S_M^0(q,t)$ of a size polydisperse system of noninteracting particles. Results for several values of s are shown as obtained using the continuous Schulz distribution.

sufficiently small, say, $s < 0.1$. This finding is mirrored in Fig. 11, where results for $\Delta_M^0(q)$ are shown for various s. As noted above, $\Delta_M^0(q)$ is very small when $s < 0.1$. Indeed, the nonexponentiality factor is maximal for $q = 0$. It is easy to show that

$$\Delta_M^0(0) = 1 - \frac{\langle \sigma^6 \rangle^2}{\langle \sigma^5 \rangle \langle \sigma^7 \rangle} \approx s^2, \tag{72}$$

with

$$\langle \sigma^n \rangle = \int_0^\infty d\sigma \, p(\sigma; \overline{\sigma}; s) \sigma^n \tag{73}$$

denoting the nth moment of the size distribution. The approximate equality on the right-hand side of Eq. (72) is valid for small s only.

The limiting case of noninteracting particles was used here as the most simple test for assessing the range of validity of the decoupling approximation. It is fair to state that, at least for noninteracting particles, the decoupling approximation is useful when $s < 0.1$. For the same range of size polydispersity, the decoupling approximation performs sufficiently well also for systems of strongly interacting particles,
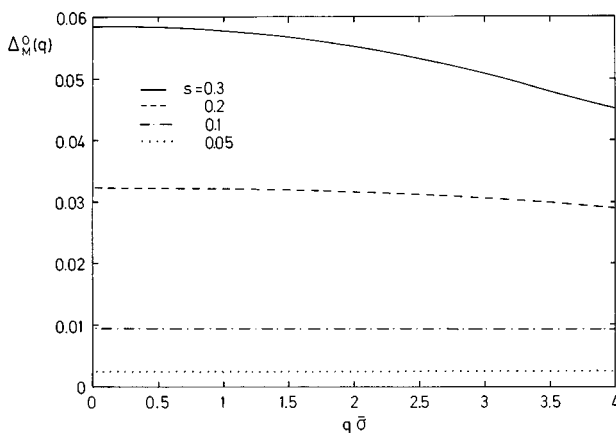

FIG. 11. Measurable nonexponentiality factor $\Delta_M^0(q)$ corresponding to Fig. 10.

as far as the calculation of the measurable static structure factor is concerned. This finding was obtained in [23] (cf. also [8]), where decoupling approximation results for $S_M(q)$ have been tested against a more sophisticated multicomponent calculation of $S_M(q)$ based on a discretized Schulz distribution of particle sizes. The dynamical properties of interacting colloidal particles are expected to be more affected by polydispersity than the static ones, which limits the range of validity of the decoupling approximation to somewhat smaller values of s. For the example of tracer diffusion, this is demonstrated also in [23].

We point out, however, that all experimental systems considered in this work are weakly polydisperse with $s \lesssim 0.06$. For these small amounts of polydispersity, we expect the decoupling approximation to be sufficiently good for the calculation of the nonexponentiality factor. For larger values of s, the decoupling approximation becomes unreliable and one has to resort to a more elaborate multicomponent description for calculating the amount of nonexponentiality. The present authors are currently extending the MCA scheme proposed in this work to substantially polydisperse systems and to mixtures.

From this discussion it should be clear that in a polydisperse sample there are two sources of nonexponential behavior of the measurable dynamic structure factor $S_M(q,t)$: the one arising from the memory effects and a trivial one that is already present when the particles are noninteracting. The above consideration of this trivial contribution $\Delta_M^0(q)$ shows that it is smaller than 0.01 for $s = 0.1$ and smaller than 0.003 for $s = 0.05$. These values for the nonexponentiality factor should be compared with the ''nontrivial'' ones calculated for the realistic systems and displayed in Figs. 4–8; these latter factors are much larger for practically all values of q. As a conclusion, the nonexponential behavior of the measurable dynamic structure factor, for the systems investigated in this paper, is almost exclusively due to the memory effects.

In the final part of this section, we investigate how the nonexponential decay of the dynamic structure factor is affected by the amount of added electrolyte. Since there is no experimental study so far concerning this interesting issue, our investigations are intended to encourage further work on it. Let us consider, e.g., the effect of adding salt to the strongly coupled sample (id83)YZ, investigated by Müller in the salt-free limit only. The calculated $\Delta_D(q)$ for $s = 0.05$ and various concentrations n_s of added 1-1 electrolyte, ranging from 0 to 100 μM, are shown in Fig. 12(a). For comparison, the corresponding results for vanishing polydispersity are displayed in Fig. 12(b). From these figures, we observe that adding salt leads to a drastic decrease in the magnitude of the nonexponential decay of the dynamic scattering functions $S(q,t)$ and $S_D(q,t)$. In particular, the local minimum (maximum) at $q \approx q_m$ ($q \approx 1.5 q_m$) is disappearing with increasing n_s.

From Fig. 13, which shows the radial distribution function $g(r)$ for values of n_s corresponding to Figs. 12(a) and 12(b), we find that the two-particle correlations become significantly reduced with increasing salt, the height of the principal peak of $g(r)$ decreases, and the peak position is shifted towards smaller distances. As a result, the correlation-induced particle caging becomes less pronounced, giving rise to a smaller nonexponentiality factor.
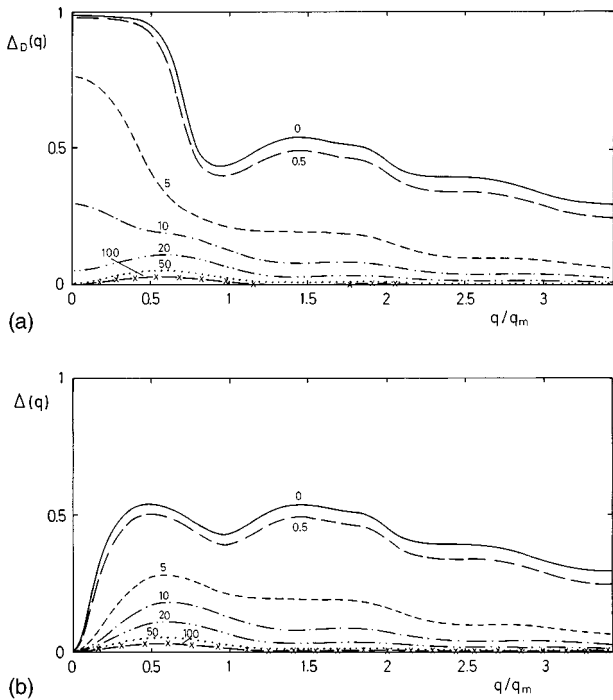
(a)

(b)

FIG. 12. (a) Nonexponentiality factor $\Delta_D(q)$ of sample id83YZ for $s=0.05$. Comparison of the theoretical results for various concentrations n_s of added 1-1 electrolyte, ranging from 0 to 100 μM. The remaining system parameters are the same as in Table I. (b) Same as in (a), but for $s=0$.

Most sensitive to the presence of salt ions is the long-wave-number limit of $\Delta_D(q)$, which strongly decreases on increasing n_s. In fact, at small q the effect of polydispersity becomes less important when salt is added, i.e., $\Delta_D(q) \approx \Delta(q)$ is found already for values of q/q_m smaller than one. This finding can easily be understood considering Eqs. (52) and (60). The small-q limits of $S(q)$ and $S_D(q)$ are very sensitive to the salt concentration as can be observed from Fig. 14, where $S(0)$ and $S_D(0)$ are found to increase on increasing n_s. Adding salt gives more weight to the first term in Eq. (52), since its magnitude and decay rate are proportional, respectively, to $S(0)$ and $S(0)^{-1}$. Thus, $\Delta_D(0)$ decreases strongly on increasing n_s.

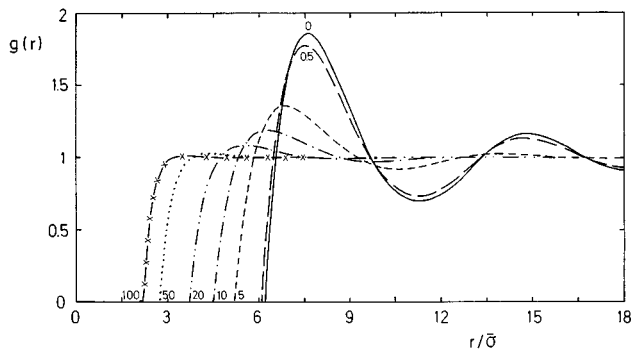We can reach the same conclusion from Eq. (60) and by noting that the relative difference $|S_D(0)-S(0)|/S(0)$ be-
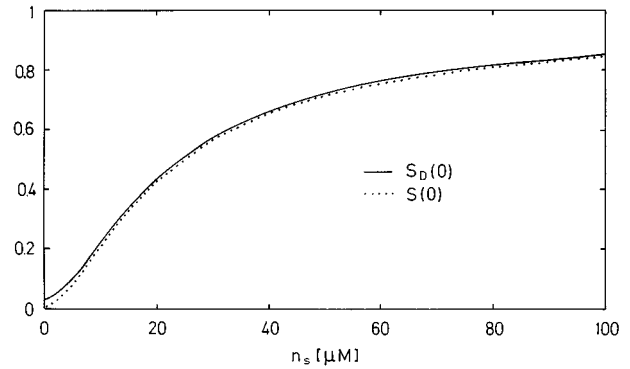

FIG. 14. RMSA results of sample id83YZ for $S_D(0)$ (solid line) and for $S(0)$ (dotted line) as functions of the concentration of added 1-1 electrolyte n_s.

tween $S_D(0)$ and $S(0)$ becomes very small at larger amounts of salt. According to Eq. (60), $\Delta_D(0)$ depends explicitly on the normalized long-time self-diffusion coefficient. Figure 15 contains our finding for D^* as a function of n_s, calculated from solving Eq. (63) for the parameters of sample (id83)YZ. The effect of adding salt is to enhance the self-diffusion at long times, i.e., for correlation times $t \gg \tau_I$.

VI. CONCLUDING REMARKS

In the present work, we have used a mode-coupling approximation for calculating the nonexponentiality factor (reduced memory function). On the basis of the decoupling approximation, we have extended the theory to moderately polydisperse suspensions. From the comparison of the theoretical results with available experimental data, the overall agreement is considered to be satisfactory. We point out again that the present treatment of the dynamics introduces no adjustable parameter. The only input is the static structure factor, which was chosen to fit the static light scattering data.

Our analysis has shown that already a very small amount of polydispersity leads to a finite value of $\Delta_D(q=0)$ in strongly correlated systems and that the effect of polydispersity on the nonexponential decay of concentration fluctuations is most pronounced at small wave numbers. Furthermore, we have found that the strength of the nonexponential decay is significantly affected by the amount of added electrolyte. Enlarging the salt concentration gives rise to smaller
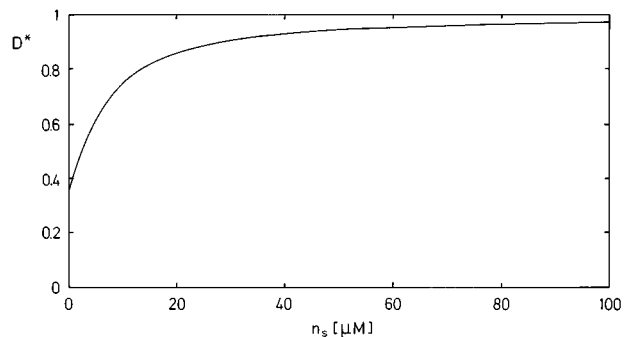

FIG. 13. RMSA results for the radial distribution function $g(r)$ for the same amounts of added 1-1 electrolyte as in Fig. 12.

FIG. 15. Mode-coupling result for the normalized long-time self-diffusion coefficient D^* of sample id83YZ as a function of n_s.

values of $\Delta_D(q=0)$ and to larger values of the long-time self-diffusion coefficient.

In spite of the good qualitative agreement found between our theoretical approach and the experiment, there remain some quantitative deviations. In particular, at larger wave numbers our MCA results have the tendency to underestimate somewhat the amount of nonexponentiality when the system is strongly correlated. The quantitative agreement with the experimental data might be further improved by attempting a full self-consistent solution of the mode-coupling scheme. However, before getting involved into this numerically very demanding task, it is necessary to investigate first the additional influence of hydrodynamic interactions on the nonexponential relaxation of $S(q,t)$. Hydrodynamic interactions have been ignored in the present work, since from the theoretical point of view it is important to understand first the effects of direct interactions on the suspension dynamics.

Effects of the hydrodynamic interactions have been frequently considered in the past to be negligible in the case of dilute suspensions of charged particles, for the reason that the strong electrostatic forces keep the particles far apart. On the other hand, recent theoretical investigations have clearly demonstrated for such suspensions that hydrodynamic interactions are important, in particular with regard to the small-q limit of the hydrodynamic function $H(q)$ [8,10,29,30] and to the long-time self-diffusion coefficient [31]. For example, for a charge-stabilized suspension the effect of hydrodynamic interactions on $H(q)$ was shown to be substantially more pronounced than for a suspension of hard spheres at the same volume fraction.

Contrary to hard sphere suspensions, where $g(r)$ attains its maximum at contact distance, i.e., at $r=\sigma^+$, $g(r)$ for charged particles remains essentially zero for separations comparable to the Debye-Hückel screening length. Therefore, in dilute charge-stabilized suspensions at sufficiently low ionic strength, it is possible to only account for the leading far-field contribution of the hydrodynamic interactions, which is pairwise additive [8,10,29]. This should be contrasted with suspensions of strongly correlated hard spheres, where one needs to consider many-body hydrodynamic interactions.

The present authors are currently extending the MCA scheme of this work to include, besides potential interactions, also the far-field contribution of the hydrodynamic interactions and to quantify its influence on $\Delta_D(q)$ and on D_s^L. Our preliminary calculations indicate that $\Delta_D(q)$ and D_s^L are indeed influenced to some extent by the hydrodynamic interactions. These calculations indicate further that our findings on the qualitative behavior of $\Delta_D(q)$ remain essentially unchanged when also hydrodynamic interparticle forces are considered.

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