

# Dynamics of Quasi Two-Dimensional Colloidal Systems

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In this paper we examine the asymptotic long time dynamics of quasi two-dimensional colloidal suspensions over a wide range of concentrations. At low concentrations the dynamics is determined by uncorrelated binary collisions among the constituent particles. These collisions among the particles lead to logarithmic corrections to the well-known linear growth in time of the mean squared displacement of the particles in the suspension. The self-scattering function of the suspension can be related to the mean squared displacement via the Gaussian approximation, which we examine in detail for systems of low concentration. At higher concentrations caging effects influence the dynamics of the suspension, which we account for by developing a formal mode coupling theory for colloidal systems from first principles. Equations for the dynamics of the memory functions that account for caging effects are derived and solved self-consistently, for the case of instantaneous hydrodynamic interactions, by utilizing the Gaussian approximation for the scattering functions of the colloidal system and assuming a particular form for the cumulants of the position. We find that the functional form suggested by Cichocki and Felderhof for the time dependence of the mean squared displacement of quasi two-dimensional colloidal systems in the limit that hydrodynamic interactions are instantaneous is compatible with the predictions of mode coupling theory. Furthermore, we explicitly evaluate the long time diffusion coefficient and other parameters as a function of concentration.

## 1. Introduction

Recent studies of quasi two-dimensional colloidal suspensions using light microscopy have provided detailed information on the dynamics of the suspension over a wide range of concentration.<sup>1–3</sup> These data provide information about the microscopic state of the system as a function of time and therefore permit direct calculation of statistical properties such as the mean squared displacement of the colloid particles. It is well-known that the mean squared displacement of an isolated Brownian particle in a three-dimensional fluid increases linearly with time. However a suspension of interacting Brownian particles demonstrates much more complicated behavior,<sup>4</sup> in which the mean squared displacements at short and long times grow linearly in time, but the mean squared displacement at intermediate time grows in a complicated fashion that depends on the volume fraction of the suspended particles and on the nature of their interactions.

Recently, much attention has been focused on quasi two-dimensional (thin cell) colloidal suspensions where the restricted geometry of the system is reflected in both static<sup>5</sup> and dynamic properties.<sup>2,6</sup> The influence of geometric restrictions on the dynamics of the suspension is an issue of much interest and debate in the scientific community. Many theorists have used the Smoluchowski operator, which is proportional to a Brownian particle transport coefficient, to derive a generalized Langevin equation that describes the dynamics of a system constrained to have a restricted geometry without considering whether the relevant transport coefficient is well-defined. It is well established that in a strictly two-dimensional system consisting of a large Brownian particle immersed in a bath of small discs the mean squared displacement, in fact, grows more strongly than linearly at long times due to mode coupling effects which describe the formation of vortex motions in the fluid.<sup>7</sup> The mode coupling effects imply that the motion of the Brownian disc in a two-dimensional system cannot be described by a

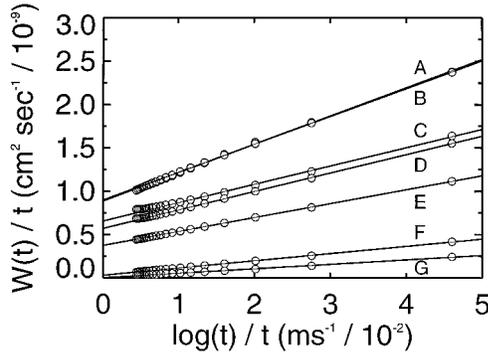
diffusion equation and that the hydrodynamic equations do not describe the dynamics of the bath of discs since the transport coefficients do not exist. In apparent contradiction with these results, several authors have successfully utilized the Smoluchowski equation, which incorporates a diffusion coefficient, in their studies of the dynamics of quasi two-dimensional suspensions and completely ignored both mode coupling effects of the bath and correlated collisions among the Brownian particles. In particular, Cichocki and Felderhof<sup>6</sup> recently investigated the self-diffusion in a semidilute suspension of interacting Brownian particles using the adjoint Smoluchowski operator to generate time displacements in the long time regime. They found that the mean squared displacement  $W(t)$  behaves for long times  $t$  as

$$W(t) = D_s^L t + (D_s^S - D_s^L) \tau_L \log(t/\tau_m) + o(1) \quad (1.1)$$

where  $D_s^L$  and  $D_s^S$  are the long and short time self-diffusion constants and  $\tau_L$  and  $\tau_m$  are time scales that depend on the nature of the interactions between Brownian particles and the volume fraction of the suspension. They claim that the logarithmic term in (1.1) is due to a  $1/t$  singularity in a memory function that is characteristic of Brownian systems in two dimensions, and hence (1.1) should apply for two-dimensional systems at any concentration. Experimentally this claim appears to have some validity, as is shown in Figure 1. Although these data are for relatively short times compared to the time required for an isolated Brownian particle to diffuse a distance of several diameters at high concentrations, the functional form is readily apparent. A description of these experiments will be published elsewhere.<sup>2</sup>

In this paper we carefully examine these issues in detail, and we develop a formal description of the dynamics of a colloidal suspension in a thin cell. Our theory develops a proper framework that incorporates the effects of both mode coupling and binary uncorrelated collisions of the Brownian particles on the memory function describing the Brownian dynamics in a simple model system of hard spheres. We demonstrate that the functional form of the dynamics of the suspension is determined

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**Figure 1.** Plot of the mean squared displacement  $W(t)$  divided by time  $t$  versus  $\log(t)/t$  at reduced areal densities  $\rho^* = n\sigma^2/A_s$ , where  $\sigma$  is the diameter of the spheres,  $n$  is the number density, and  $A_s$  is the area of the system. The letters in the diagram correspond to the reduced areal density values  $A = 0.08$ ,  $B = 0.24$ ,  $C = 0.50$ ,  $D = 0.58$ ,  $E = 0.69$ ,  $F = 0.84$ , and  $G = 0.88$ .

principally by the binary collisions, although the mode coupling has significant effects on the long time self-diffusion constant of the system.

The paper is organized as follows: In section 2 the model system is introduced and a systematic method of calculating correlation functions involving only Brownian particle degrees of freedom is presented. We derive the Fokker–Planck operator for time displacements of the Brownian degrees of freedom at times greater than the time scale for decay of the bath particle correlations. In section 3 we present the mode coupling formalism; it is based upon  $N$  ordering techniques developed elsewhere.<sup>8</sup> We formulate an expression for the generalized collective and self-diffusion coefficients and derive self-consistent equations for the memory functions that appear in the expressions for the generalized diffusion coefficients. We then examine these expressions in the asymptotic long time diffusive regime where correlations involving the momenta have decayed, and we calculate the self-diffusion coefficient. At low concentrations the mode coupling effects are small and the self-diffusion coefficient is determined mainly by binary uncorrelated collisions. At higher concentrations, where the mode coupling effects are significant, we investigate the compatibility of a functional form proposed by Cichocki and Felderhof<sup>6</sup> (eq 1.1) for the time dependence of the mean squared displacement with mode coupling theory. We find that although the mode coupling effects significantly decrease the magnitude of the long time self-diffusion coefficient, the effects are established rapidly and to a good approximation do not alter the functional dependence on the time of the mean squared displacement. In section 4 we summarize these results.

## 2. Fokker–Planck Dynamics

The quasi two-dimensional colloidal system consists of  $N$  identical massive spherical particles of radius  $a$  whose center of mass coordinates and momenta are denoted by  $\mathbf{R}^N$  and  $\mathbf{P}^N$ , respectively, where  $\mathbf{R}^N$  and  $\mathbf{P}^N$  are  $2N$ -dimensional vectors with components  $\mathbf{R}_j$  and  $\mathbf{P}_j$  with  $j = 1, \dots, N$ . The colloid particles are immersed in a simple fluid composed of  $N^*$  small molecules and the entire system is confined between two plates. The geometry of the system restricts the center of mass motion of the colloid particles to a plane, but allows the solvent molecules to move in three dimensions. We denote the phase point for the colloid degrees of freedom by  $X \equiv (\mathbf{R}^N, \mathbf{P}^N)$  and the phase point for the solvent degrees of freedom by  $X_b \equiv (\mathbf{r}^{N^*}, \boldsymbol{\pi}^{N^*})$ .

The Hamiltonian for the system can be written in the form

$$H(X, X_b) = H_B(X) + H_b(X_b) + \phi(X, X_b) \quad (2.1)$$

where  $H_B$  is the Hamiltonian for the isolated colloid particles,

$H_b$  is the Hamiltonian for the isolated bath molecules, and  $\phi$  describes the interactions between the bath and colloid particles. The Hamiltonian  $H_B$  has the form

$$H_B(X) = \frac{\mathbf{P}^N \cdot \mathbf{P}^N}{2M} + U(\mathbf{R}^N) \quad (2.2)$$

where  $M$  is the mass of the colloid particles and  $U$  can be written as a sum of two-body short-ranged potentials,

$$U(\mathbf{R}^N) = \sum_{i=1}^N \sum_{j>i} U(R_{ij}) \quad (2.3)$$

where  $R_{ij} \equiv |\mathbf{R}_i - \mathbf{R}_j|$ . The Hamiltonian  $H_b$  is of the form

$$H_b = \sum_{j=1}^{N^*} \left( \frac{\boldsymbol{\pi}_j \cdot \boldsymbol{\pi}_j}{2m} + V(r_j) \right) \quad (2.4)$$

The Liouville operator for the system can be written as

$$L = L_B + L_b + L_\phi \quad (2.5)$$

where

$$L_B = -\frac{\mathbf{P}^N}{M} \cdot \nabla_{\mathbf{R}^N} + \nabla_{\mathbf{R}^N} U \nabla_{\mathbf{P}^N}$$

$$L_b = -\frac{\boldsymbol{\pi}^{N^*}}{m} \cdot \nabla_{\mathbf{r}^{N^*}} + \nabla_{\mathbf{r}^{N^*}} V \nabla_{\boldsymbol{\pi}^{N^*}} \quad (2.6)$$

and

$$L_\phi = \nabla_{\mathbf{R}^N} \phi \nabla_{\mathbf{P}^N} + \nabla_{\mathbf{r}^{N^*}} \phi \nabla_{\boldsymbol{\pi}^{N^*}} \quad (2.7)$$

The Liouville operator  $L$  determines the time evolution of an arbitrary function of the variables of the system,  $C(X, X_b)$ , according to

$$C(X, X_b; t) = e^{-Lt} C(X, X_b) \quad (2.8)$$

We are interested in the long time behavior of correlation functions of dynamical variables which are defined in the colloid phase space  $X$ , such as

$$F(k, t) = \frac{\langle \hat{N}(k, t) \hat{N}(k)^* \rangle_\rho}{NS(k)} = \frac{\langle [e^{-Lt} \hat{N}(k)] \hat{N}(k)^* \rangle_\rho}{NS(k)} \quad (2.9)$$

where  $S(k)$  is the structure factor for the colloid particles,

$$\hat{N}(k) = (1 - \delta_{k,0}) \sum_{j=1}^N e^{-ik \cdot \mathbf{R}_j} \quad (2.10)$$

and  $\langle B \rangle_\rho$  denotes the average of  $B(X)$  over the equilibrium distribution function of the system

$$\rho_e = \frac{e^{-\beta H} e^{-\beta H_b} e^{-\beta \phi}}{q} \quad (2.12)$$

where

$$q \equiv \int dX dX_b e^{-\beta H} e^{-\beta H_b} e^{-\beta \phi}$$

In eq 2.12 we have used the conventional notation  $\beta \equiv (K_B T)^{-1}$ , with  $T$  being the temperature of the overall system. We define

the reduced distribution function for the colloid subsystem  $W_e$  by integrating  $\rho_e$  over the bath phase space,

$$W_e(\mathbf{R}^N, \mathbf{P}^N) = \int dX_b \rho_e(X, X_b) \quad (2.12)$$

and define  $\tilde{\rho}(\mathbf{R}_N, X_b)$  to be the conditional distribution function for the bath molecules in the presence of fixed colloid particles;

$$\tilde{\rho} \equiv \rho_e / W_e \quad (2.13)$$

Note that  $\tilde{\rho}$  is normalized in the sense that  $\int dX_b \tilde{\rho} = 1$ . Since  $\rho_e = \tilde{\rho} W_e$ , we may write for a correlation function involving dynamical variables of the  $X$  phase space

$$\langle [e^{-Lt} A(X)] B(X) \rangle_\rho = \langle [e^{-Lt}]_b A(X) B(X) \rangle \quad (2.14)$$

where  $\langle f(X, X_b) \rangle_b = \int dX_b \tilde{\rho}(\mathbf{R}_N, X_b) f(X, X_b)$  and  $\langle B(X) \rangle = \int dX B(X) W_e(X)$ . Using projection operator techniques,<sup>8</sup> it is straightforward to establish that

$$\int_0^\infty dt e^{-zt} \langle e^{-Lt} \rangle_b = \int_0^\infty dt e^{-zt} \Xi(t) = \tilde{\Xi}(z) = \frac{1}{z - \mathcal{O}(z)} \quad (2.15)$$

where

$$\mathcal{O}(z) = -\nabla_{\mathbf{R}^N} (U + \omega) \cdot \nabla_{\mathbf{P}^N} + \frac{\mathbf{P}^N}{M} \cdot \nabla_{\mathbf{R}^N} + \sum_{ij} \left( \nabla_{\mathbf{p}^i} - \frac{\beta}{M} \mathbf{P}_i \right) \cdot \tilde{\Gamma}_{ij}(\mathbf{R}^N, z) \cdot \nabla_{\mathbf{p}^j} \quad (2.16)$$

In eq 2.16,  $\omega(\mathbf{R}^N)$  is the potential of mean force,

$$e^{-\beta\omega(\mathbf{R}^N)} = \int dX_b \rho_b(X_b) e^{-\beta\phi} \quad (2.17)$$

where  $\rho_b$  is the equilibrium distribution function for the isolated bath molecules. The generalized friction coefficient  $\tilde{\Gamma}_{ij}(\mathbf{R}^N, z)$  is defined by the correlation function

$$\tilde{\Gamma}_{ij}(\mathbf{R}^N, z) = \int_0^\infty dt e^{-zt} \langle [e^{-\mathcal{L}_b t} \hat{\nabla}_{\mathbf{R}_i} \phi] \hat{\nabla}_{\mathbf{R}_j} \phi \rangle_b \quad (2.18)$$

where  $\mathcal{L}_b = (1 - \mathcal{R}_b)$ ,  $\hat{\nabla}_{\mathbf{r}} \phi = \nabla_{\mathbf{R}}(\phi - \omega)$ , and  $\mathcal{R}_b B(X) = \langle B(X) \rangle_b$ . Defining the small parameter  $\epsilon^2 = m/M$ , the generalized friction coefficient can be approximated as<sup>8</sup>

$$\tilde{\Gamma}_{ij}(\mathbf{R}^N, z) = \int_0^\infty dt e^{-zt} \langle [e^{-L_0 t} \hat{\nabla}_{\mathbf{R}_i} \phi] \hat{\nabla}_{\mathbf{R}_j} \phi \rangle_b + O(\epsilon) \quad (2.19)$$

where  $L_0 = L_b + \nabla_{\mathbf{r}^N} \phi \nabla_{\mathbf{r}^N}$ . If bath molecule correlations decay on a time scale  $\tau_b$  that is short relative to the time scale of the decay of colloid particle correlations, then for  $t \gg \tau_b$

$$\Xi(t) \approx e^{\mathcal{O}t} \quad (2.20)$$

where  $\mathcal{O}$  is the Fokker–Planck operator,

$$\mathcal{O} = -\nabla_{\mathbf{R}^N} (U + \omega) \cdot \nabla_{\mathbf{P}^N} + \frac{\mathbf{P}^N}{M} \cdot \nabla_{\mathbf{R}^N} + \sum_{ij} \left( \nabla_{\mathbf{p}^i} - \frac{\beta}{M} \mathbf{P}_i \right) \cdot \tilde{\Gamma}_{ij}(\mathbf{R}^N, z=0) \cdot \nabla_{\mathbf{p}^j} \quad (2.21)$$

These results suggest that when  $t \gg \tau_b$  the time evolution of colloid particle correlation functions is determined by the Fokker–Planck operator  $\mathcal{O}$  according to

$$\langle A(X; t) B(X) \rangle_\rho = \langle [e^{\mathcal{O}t} A(X)] B(X) \rangle \quad (2.22)$$

where  $A(X)$  and  $B(X)$  are arbitrary dynamical variables of the colloid particle phase space. It should be noted that in a strictly two-dimensional system of colloid discs and solvent discs the friction coefficient  $\tilde{\Gamma}_{ij}(\mathbf{R}^N, z)$  does not exist as  $z$  approaches zero due to mode coupling effects; in that case no separation of time scales exists between bath particle and colloid particle correlation function decays. For finite and three-dimensional systems the coupling of bath particle modes to colloid particle motion yields finite contributions and allows the  $z = 0$  friction coefficient to be related to properties of the solvent, such as its viscosity. These “hydrodynamic” interactions also lead to a complicated functional dependence of  $\tilde{\Gamma}_{ij}(\mathbf{R}^N, z)$  on the spatial positions  $\mathbf{R}^N$  of the colloid particles;<sup>9</sup> they are known to be important in determining the transport properties of colloid systems.<sup>10</sup>

Throughout this paper we will assume that the hydrodynamic interactions occur on a time scale much shorter than the time scale of interactions among the colloid particles and hence will be treated as instantaneous. Medina-Noyola<sup>21</sup> has suggested a simple picture of the dynamics of suspensions in which between collisions a colloid particle diffuses in a static field of its neighbors. The presence of other particles modifies only the effective friction a particle feels while diffusing, hence the identification

$$\langle \tilde{\Gamma}_{ij} \rangle = \delta_{ij} \mathbf{I} \frac{(K_B T)^2}{D_s^s(\phi)} \quad (2.23)$$

is made, where  $D_s^s(\phi)$  is the density dependent “short time” self-diffusion coefficient. The short time diffusion coefficient determines the dynamics of the self-scattering  $F_s(k, t)$  for times shorter than  $\tau_l$ , the average time a colloid particle requires to diffuse a mean separation distance between colloid particles in the suspension. Typically, one expects  $\tau_l \approx 1/nD_0 \gg MK_b T / \tilde{\Gamma}$ , where  $D_0$  is the diffusion coefficient for an isolated colloid particle in solution. Ideally,  $D_s^s(\phi)$  can be calculated given a particular model, but in practice it is simpler to determine  $D_s^s(\phi)$  empirically from fitted data. In the following sections we leave  $(K_b T)^2 / \tilde{\Gamma}_{ij} \equiv \mathbf{I} \delta_{ij} D$  unspecified, keeping in mind that  $D$  should be closely related to  $D_s^s(\phi)$ .

### 3. Projection Operator Formalism and Mode Coupling

In this section we develop a systematic mode coupling formalism that in principle allows the transport properties and dynamics of colloid suspensions of arbitrary concentration to be calculated. Our view of the dynamics of colloid suspensions borrows heavily from knowledge of the character of the long time dynamics of collective excitations in hard sphere liquids. Over the last 15 years considerable progress has been made in the study of hard sphere liquids. de Schepper, Cohen, and co-workers have established the existence of short-wavelength collective excitations in hard sphere liquids that determine the dynamic scattering function  $F(k, t)$  at intermediate times (i.e. on the order of 10 collision times).<sup>11</sup> They have shown that these collective excitations, which are extensions to nonzero wavevector of the hydrodynamic modes of the fluid, give important mode coupling contributions and are essential for the proper description of the dynamics of density fluctuations at intermediate times. The important physical parameters that characterize the collective excitations are the density  $n$  and the mean-free-path  $l$ . The collective excitations lose their significance when  $kl \geq 1$ . At high concentrations we generally expect  $l \gg a$ , where  $a$  is the radius of the hard sphere; hence collective excitations are important in concentrated colloid systems even for  $ka \approx 1$ .

Generally it is assumed that the long time behavior of density fluctuations is determined by a set of slow modes of the system. Initially it was thought that the only slow modes of a liquid system were the densities of the conserved quantities of the system in the small wavevector regime. The long time behavior of the system can then be represented in terms of the dynamics of those important "hydrodynamic" densities.<sup>13</sup> It is now apparent that in dense systems collective modes extended to large wavevectors, up to  $K_c \approx 1/l$ , are still slower than the other "kinetic" modes of the system, which implies that the cutoff wavevector  $K_c$  is larger than initially thought to be the case. This realization helps explain why the magnitude of the long time tail of a correlation function calculated in a molecular dynamics simulation is, typically, much larger than the first mode coupling calculations predicted.<sup>12</sup>

In analogy with hard sphere liquid systems, we shall assume that the long time dynamics of the density fluctuations in colloid suspensions is determined by the extensions of the conserved hydrodynamic densities to larger "nonhydrodynamic" wavevectors. For the colloid suspension these variables are the number density  $\hat{N}(k) = (1 - \delta_{k,0}) \sum_{j=1}^N e^{-i\mathbf{k}\cdot\mathbf{R}_j}$  and the momentum density  $\mathbf{P}(k) = \sum_{j=1}^N \mathbf{P}_j e^{-i\mathbf{k}\cdot\mathbf{R}_j}$ . We define our complete set of slow variables to be  $A(k) = \{\hat{N}(k), \mathbf{P}(k)\}$  and

$$\begin{aligned} Q_0 &= 1 \\ Q_1(k) &= A(k) \end{aligned} \quad (3.1)$$

$$\begin{aligned} Q_2(k, q) &= A(k-q) A(q) - \\ &\langle A(k-q) A(q) Q_1(k)^* \rangle K_{11}(k)^{-1} Q_1(k) - \langle A(k-q) A(q) \rangle \delta_{k,0} \\ &\quad \vdots \end{aligned}$$

where  $K_{11}(k) = \langle Q_1(k) Q_1(k)^* \rangle$ . The subtractions are included in (3.1) to ensure that the basis set is orthogonal in mode order in the sense that  $K_{\alpha\beta} = \langle Q_\alpha Q_\beta^* \rangle = \delta_{|\alpha|, |\beta|} K_{\alpha\beta}$ . We define the projection operators  $\mathcal{P}_1$  and  $\mathcal{P}$  by

$$\begin{aligned} \mathcal{P}_1 B(k) &= \langle B(k) Q_1(k)^* \rangle K_{11}(k)^{-1} Q_1(k) \\ \mathcal{P} B(k) &= \langle B(k) Q^* \rangle K^{-1} Q \end{aligned} \quad (3.2)$$

where the \* notation denotes a sum over mode orders, over repeated wavevectors, and over hydrodynamic (i.e.  $N$  and  $\mathbf{P}$ ) indices. We now apply the operator identity

$$e^{(A+B)t} = e^{At} + \int_0^t d\tau e^{A(t-\tau)} B e^{(A+B)\tau} \quad (3.3)$$

to the expressions  $\exp(1 - \mathcal{P}_1)t$  and  $\exp(1 - \mathcal{P})t$ , and we obtain<sup>13</sup>

$$\begin{aligned} \langle Q(z) Q^* \rangle &= \int_0^\infty dt e^{-zt} \langle Q(t) Q^* \rangle = [z\mathbf{I} - \mathbf{M}(z)]^{-1} * K \\ \langle A(k, z) A(k)^* \rangle &= [z\mathbf{I} - \tilde{\mathbf{M}}(k, z)]^{-1} K_{11}(k) = \\ &= [z\mathbf{I} - \mathbf{M}(z)]_{11}^{-1} K_{11}(k) \end{aligned} \quad (3.4)$$

where

$$\mathbf{M}(z) = \langle [\mathcal{O} Q] Q^* \rangle K^{-1} - \langle \tilde{\phi}(z) Q^* \rangle K^{-1} \quad (3.5)$$

$$\tilde{\mathbf{M}}(k, z) = \langle [\mathcal{O} A(k)] A(k)^* \rangle K_{11}(k)^{-1} - \langle \tilde{f}(k, z) A(k)^* \rangle K_{11}(k)^{-1} \quad (3.6)$$

and

$$\phi(t) = \mathcal{O} e^{(1-\mathcal{P})\mathcal{O}t} (1 - \mathcal{P}) \mathcal{O} Q \quad (3.7)$$

$$f(k, t) = \mathcal{O} e^{(1-\mathcal{P})\mathcal{O}t} (1 - \mathcal{P}) \mathcal{O} A(k) \quad (3.8)$$

Noting that  $Q_1(k) = A(k)$ , we find for the Fourier–Laplace transform of the scattering function  $F(k, t)$

$$\tilde{F}(k, z) = \frac{1}{z + k^2 \tilde{D}(k, z)} \quad (3.9)$$

with a generalized collective "diffusion" coefficient

$$\tilde{D}(k, z) = \frac{K_b T}{MS(k)} \frac{1}{z + (1/mK_b T) (\gamma_1(k) + \tilde{\eta}(k, z)/n)} \quad (3.10)$$

and

$$\gamma_1(k) = \frac{1}{2N} \langle [\mathcal{O} \mathbf{P}(k)] \cdot \mathbf{P}(k)^* \rangle \quad (3.11)$$

$$\tilde{\eta}(k, z) = \frac{-1}{2L^d} \langle \tilde{f}(k, z) \cdot \mathbf{P}(k)^* \rangle$$

Using the facts that

$$\mathcal{O} \hat{N}(k) = -\frac{i\mathbf{k}}{M} \cdot \mathbf{P}(k) \quad (3.12)$$

$$\begin{aligned} \mathcal{O} \mathbf{P}(k) &= \sum_{j=1}^N \left[ -\frac{i\mathbf{k}}{M} \cdot \mathbf{P}_j \mathbf{P}_j + \mathbf{F}_j \right] e^{-i\mathbf{k}\cdot\mathbf{R}_j} - \\ &= \frac{\beta}{M} \sum_{i,j} \mathbf{P}_i \cdot \tilde{\Gamma}_{ij} e^{-i\mathbf{k}\cdot\mathbf{R}_j} = \mathbf{K}(k) = -i\mathbf{k} \cdot \boldsymbol{\tau}(k) - \gamma_2(k) \end{aligned}$$

we find

$$\begin{aligned} \gamma_1(k) &= \frac{1}{2N} \sum_{ij} Tr \langle \tilde{\Gamma}_{ij} e^{-i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_j)} \rangle \\ \tilde{\eta}(k, z) &= -\frac{1}{2L^d} \int_0^\infty dt e^{-zt} \langle [e^{(1-\mathcal{P})\mathcal{O}t} \mathbf{K}_1^D(k)] \cdot \mathbf{K}_1^D(k)^* \rangle \end{aligned} \quad (3.13)$$

where  $\mathbf{K}_1^D(k) = (1 - \mathcal{P}_1) \mathbf{K}(k)$ . When the hydrodynamic interactions are instantaneous  $\tilde{\Gamma}_{ij} = \mathbf{I} \delta_{ij} \tilde{\Gamma}$ , and  $\gamma_1(k) = \tilde{\Gamma}$ ,  $\mathbf{K}_1^D(k) = -i\mathbf{k} \cdot (1 - \mathcal{P}_1) \boldsymbol{\tau}(k)$ . Since  $\boldsymbol{\tau}(k)$  is the stress tensor for the colloid particle suspension, we see that  $\tilde{\eta}(k, z)$  is proportional to  $k^2$  times the Green–Kubo expression for the viscosity of the suspension.

Mode coupling equations can be systematically derived by applying  $N$  ordering techniques to the generalized hydrodynamic matrix  $\mathbf{M}(z)$  in eq 3.5, noting that the multilinear matrix  $\mathbf{M}_{\alpha\beta}(z)$  can be factorized for the colloid subsystem in the same way as for a simple liquid or granular system. The nonlinear Fokker–Planck time displacement operator does not alter the analysis since it can be shown that terms such as

$$\sum_{ij} \nabla_{\mathbf{R}_i} A(k-q) \cdot \tilde{\Gamma}_{ij} \cdot \nabla_{\mathbf{R}_j} A(q) \quad (3.14)$$

are negligible in  $N$  order compared to terms such as  $(\mathcal{O} A(k-q)) A(q)$ . Details of the  $N$  ordering formalism can be found in ref 13. Using the  $N$  ordering technique, a self-consistent expression for the transport coefficient  $\tilde{\eta}(k, z)$  can be obtained by expanding the multilinear correlation functions in terms of the parameter  $M/N \approx (K_c \psi)^2$ , where  $\psi$  is the correlation length of the two-dimensional system. The series is formally

resummed to yield a self-consistent expression for  $\tilde{\eta}(k, z)$ . The mode coupling series can be written as

$$\tilde{\eta}(k, z) = \tilde{\eta}^B(k, z) + \tilde{\eta}^{\text{MC}}(k, z) \quad (3.15)$$

where

$$\tilde{\eta}^B(k, z) = -\frac{1}{2L^d} \int_0^\infty dt e^{-zt} \langle [e^{(1-\mathcal{P})\mathcal{O}t} \mathbf{K}^D(k)] \cdot \mathbf{K}^D(k)^* \rangle \quad (3.16)$$

has all the projections onto the set of slow variables  $\mathcal{Q}$  removed from its fluctuating force  $\mathbf{K}^D(k) = (1 - \mathcal{P})\mathbf{K}(k)$ . Note that, in contrast,  $\mathbf{K}_1^D(k)$  has only the linear projections of the slow variables removed from  $\mathbf{K}(k)$ . The mode coupling term may be represented as an infinite series of terms written either in self-consistent form or in an expansion in powers of  $M/N$ . In self-consistent form this series looks like

$$\tilde{\eta}(k, z) = \sum_{i=2}^{\infty} \Theta_{PP}^{(i)}(k, z) \quad (3.17)$$

where

$$\Theta_{PP}^{(2)}(k, z) = \sum_{|\alpha_1|=2}^{\infty} X_{P\alpha_1} * G_{\alpha_1}(z) \cdot X_{\alpha_1 P} \quad (3.18)$$

$$\Theta_{PP}^{(3)}(k, z) = \sum_{|\alpha_1|=1, |\alpha_2|=2}^{\infty} X_{P\alpha_1} * G_{\alpha_1}(z) \cdot X_{\alpha_1 \alpha_2} * G_{\alpha_2}(z) \cdot X_{\alpha_2 P}$$

⋮

where the vertex  $X_{\alpha\beta}$  is defined to be  $\mathbf{M}_{\alpha\beta}(z)$  with at least one wavevector inequality between the sets  $\alpha$  and  $\beta$ . The propagators  $G_\alpha(z)$  are the Laplace transforms of products of the full hydrodynamic correlation functions such as  $F(k, t)$ ,  $\langle \mathbf{P}(k, t) \mathbf{P}(k)^* \rangle$ , and  $\langle \mathbf{P}(k, t) \dot{N}(k)^* \rangle$ . The vertices  $X_{\alpha\beta}$  contain static parts that are expressible in terms of static correlation functions and “dissipative” parts which resemble transport coefficients. The simplest mode coupling terms involves only the bilinear modes and is given by

$$\frac{\tilde{\eta}^{\text{MC}}(k, z)}{MK_b T} = \frac{L^d}{(2\pi)^d} \int d\mathbf{q} \frac{\hat{M}_{P;NN}^E(k, q) \hat{M}_{NN;P}^E(k, q)}{z + (\mathbf{k} - \mathbf{q})^2 \tilde{D}^B(k - q, z) + q^2 \tilde{D}^B(q, z)} \quad (3.19)$$

where  $\tilde{D}^B(k, z)$  is defined by (3.10) with  $\tilde{\eta}(k, z) = \tilde{\eta}^B(k, z)$ . The mode coupling series can also be formally resummed to obtain self-consistent equations for the transport coefficients. For example, the simplest bilinear contribution in self-consistent form is

$$\frac{\eta^{\text{MC}}(k, t)}{MK_b T} = \frac{L^d}{(2\pi)^d} \int d\mathbf{q} \hat{M}_{P;NN}^E(k, q) \hat{M}_{NN;P}^E(k, q) F(k - q, t) F(q, t) \quad (3.20)$$

This bilinear term is the most important in determining the nonanalytic  $k$  and  $z$  dependence of  $\tilde{\eta}(k, q)$  in generalized hydrodynamics, as it gives the leading  $k$  and  $z$  contributions and is responsible for the  $t^{-d/2}$  long time tail in a  $d$ -dimensional

simple liquid system.<sup>13</sup> For the suspension, the static vertices in eqs 3.19 and 3.20 are given by

$$\hat{M}_{P;NN}^E(k, q) = \frac{\langle (\mathcal{O} \mathbf{P}(k)) \mathcal{Q}_{NN}(k - q, q)^* \rangle}{N^2 S(k - q) S(q)} \quad (3.21)$$

$$\hat{M}_{NN;P}^E(k, q) = \frac{\langle (\mathcal{O} \mathcal{Q}_{NN}(k - q, q)) \mathbf{P}(k)^* \rangle}{NMK_b T}$$

The analysis just elaborated for the scattering function  $F(k, t)$  can be extended to tagged particle correlations like the Fourier transform of the van-Hove self-correlation function

$$F_s(k, t) = \langle \hat{N}_1(k, t) \hat{N}_1(k)^* \rangle = \langle e^{-i\mathbf{k} \cdot (\mathbf{R}_1(t) - \mathbf{R}_1(0))} \rangle \quad (3.22)$$

Applying the projection operator and mode coupling formalism to the Laplace transform  $F_s(k, t)$  gives

$$\tilde{F}_s(k, z) = \frac{1}{z + k^2 \tilde{D}_s(k, z)} \quad (3.23)$$

$$\tilde{D}_s(k, z) = \frac{K_b T}{M} \frac{1}{z + (\beta/M) \langle \tilde{\Gamma}_{11} \rangle + \tilde{\eta}_s(k, z)} \quad (3.24)$$

where

$$\tilde{\eta}_s(k, z) = -\int_0^\infty dt \frac{e^{-zt}}{2L^d} \langle [e^{(1-\mathcal{P})\mathcal{O}t} \mathbf{K}_s^{D+}(k)] \cdot \mathbf{K}_s^{D-}(k)^* \rangle$$

$$\mathbf{K}_s^{D\pm}(k) = (1 - \mathcal{P}_1) \left[ \frac{-i\mathbf{k} \cdot \mathbf{P}_1 \mathbf{P}_1 \pm \mathbf{F}_1}{M} \right] e^{-i\mathbf{k} \cdot \mathbf{R}_1} - (1 - \mathcal{P}_1) \gamma_2^s(k) \quad (3.25)$$

with

$$\gamma_2^s(k) = \frac{\beta}{M} \sum_{i=1}^N \mathbf{P}_i \cdot \tilde{\Gamma}_{i1} e^{-i\mathbf{k} \cdot \mathbf{R}_1} \quad (3.26)$$

Again when the hydrodynamic interactions are instantaneous,  $\tilde{\Gamma}_{ij} = \delta_{ij} \tilde{\Gamma}$ ,  $(1 - \mathcal{P}_1) \gamma_2^s(k) = 0$ , and  $\langle \tilde{\Gamma}_{11} \rangle = \tilde{\Gamma}$ , and the tagged particle transport coefficient  $\tilde{\eta}_s(k, z)$  has a term of order  $k^0$ , unlike the  $N$  particle transport coefficient  $\tilde{\eta}(k, z)$ , which is at least of order  $k^2$ . This difference is due to the fact that the instantaneous force on an individual particles is nonzero even though the total instantaneous force on the system is always zero for a conservative system.

Mode coupling equations can be derived for the tagged particle transport terms in a manner analogous to that presented above.<sup>14</sup> We find that the simplest bilinear mode coupling term in self-consistent form is

$$\frac{\eta_s^{\text{MC}}(k, t)}{MK_b T} = \frac{L^d}{(2\pi)^d} \int d\mathbf{q} \hat{M}_{P_1;N_1N}^{\text{SE}}(k, q) \hat{M}_{N_1N;P_1}^{\text{SE}}(k, q) F_s(k - q, t) F(q, t) \quad (3.27)$$

where

$$\hat{M}_{P_1;N_1N}^{\text{SE}}(k, q) = \frac{\langle [\mathcal{O} \mathbf{P}_1(k)] \mathcal{Q}_{N_1N}(k - q, q)^* \rangle}{NS(q)} \quad (3.28)$$

$$\hat{M}_{N_1N;P_1}^{\text{SE}}(k, q) = \frac{\langle [\mathcal{O} \mathcal{Q}_{N_1N}(k - q, q)] \mathbf{P}_1(k)^* \rangle}{MK_b T} \quad (3.29)$$

Note that, through (3.27), the dynamics of  $F_s(k, t)$  is related to the dynamics of the  $N$ -particle correlation function  $F(k, t)$ . When the hydrodynamic interactions are instantaneous, we find the products of the tagged particle and  $N$ -particle vertices are given by

$$\hat{M}_{P_1, N_1 N}^{\text{SE}}(k, q) \hat{M}_{N_1 N, P_1}^{\text{SE}}(k, q) = \frac{K_b T (nqh(q))^2}{MN(1 + nh(q))} \quad (3.30)$$

$$\hat{M}_{P, NN}^{\text{E}}(k, q) \hat{M}_{NN, P}^{\text{E}}(k, q) = \frac{K_b T n^2}{MN} S(|\mathbf{k}-\mathbf{q}|) S(q) ((\mathbf{k}-\mathbf{q})C(|\mathbf{k}-\mathbf{q}|) + \mathbf{q}C(q))^2 \quad (3.31)$$

where in eq 3.31 we have approximated the three-point correlation function with the relation

$$\langle \hat{N}(k) \hat{N}(k-q)^* \hat{N}(q)^* \rangle \approx NS(|\mathbf{k}-\mathbf{q}|) S(q) S(k) \quad (3.32)$$

In eq 3.30,  $N$  is the total number of colloid particles in the system,  $n = N/L^d$  is the number density of colloid particles,  $nh(q) = S(q) - 1$ , and  $C(q) = 1/n - 1/(nS(q))$  is the direct correlation function of the colloid system. Note that as  $q$  grows large, the vertex functions approach zero and hence naturally cutoff the integral over the wavevector at large  $q$ . It should be noted that eq 3.20 for  $\eta^{\text{MC}}(k, t)$  has been derived systematically and is identical in form to the mode coupling equations derived by Szamel and Lowen in their discussion of the glass transition in colloid systems.<sup>18</sup>

The mode coupling terms are designed to take into consideration the fact that at intermediate to high densities each particle is surrounded by a cage of others, which leads to correlated collisions and collective vortex motions in the suspension. The “bare” term  $\tilde{\eta}_{(s)}^{\text{B}}(k, z)$  has all the correlated motion removed from its fluctuating force  $\mathbf{K}_{(s)}^{\text{D}}(k, t)$  via the projection operator  $(1 - \mathcal{P})$  and hence can be thought of as having its dynamics determined by uncorrelated binary collisions alone. For low-density systems the upper cutoff  $K_c$  is small since the mean distance over which a particle diffuses before colliding with another particle is large, and hence one expects the mode coupling contributions to be negligible. As the density increases the cutoff increases and the vertex functions contain more significant structure, which in turn implies that the mode coupling terms become important. Near the close packed density one anticipates that the feedback mechanism can lead to anomalous increases in the memory term of the generalized friction coefficient and can provide a mechanism for critical slowing down and glass formation.

#### 4. Hard Sphere Dynamics in the Diffusive Regime

**4.1. Low-Density Systems.** To solve the hierarchy of equations for the correlation functions  $F_s(k, t)$  and  $F(k, t)$ , some approximate form of the bare memory functions  $\tilde{\eta}_{(s)}^{\text{B}}(k, z)$  must be adopted. The simplest sensible approximation for the bare memory function is to use the low-density form for all densities. We shall concern ourselves mainly with correlation functions in the “diffusive” time regime  $t \gg \tau_D$ , where  $\tau_D = M/\beta\tilde{\Gamma}$ , and assume that the hydrodynamic interactions are instantaneous. This time scale is the so-called “overdamped” limit in which

terms of order  $z\tau_D$  are ignored,<sup>15,16</sup> and it corresponds to setting

$$\tilde{D}_s(k, z) = \frac{(K_b T)^2}{\tilde{\Gamma} + \tilde{\eta}_s(k, z)} = D \frac{\tilde{\Gamma}}{\tilde{\Gamma} + \tilde{\eta}_s(k, z)}$$

$$\tilde{D}(k, z) = \frac{(K_b T)^2}{S(k)} \frac{1}{\tilde{\Gamma} + \tilde{\eta}(k, z)/n} = \frac{D}{S(k)} \frac{\tilde{\Gamma}}{\tilde{\Gamma} + \tilde{\eta}(k, z)/n} \quad (4.1)$$

in eqs 3.10 and 3.23, where we have defined  $D = (K_b T)^2/\tilde{\Gamma}$ . Furthermore, we shall assume that correlation functions involving momenta of the particles decay more rapidly than do correlation functions that involve only spatial coordinates. Under these conditions we find that, by averaging over the momenta of the system,

$$\tilde{\eta}^{\text{B}}(k, z)/n = \frac{k^2}{2L^d} \int_0^\infty dt e^{-zt} \langle [e^{\mathcal{Q}_N \Omega^\dagger t} \tau_l^{\text{UD}}(k)] \cdot \tau_l^{\text{UD}}(k)^* \rangle$$

$$\tilde{\eta}_s^{\text{B}}(k, z) = \frac{1}{2L^d} \int_0^\infty dt e^{-zt} \langle [e^{\mathcal{Q}_N \Omega^\dagger t} \mathbf{F}_1^{\text{D}}(k)] \cdot \mathbf{F}_1^{\text{D}}(k)^* \rangle \quad (4.2)$$

where  $\mathcal{Q}_N = (1 - \mathcal{P}_N)$  removes the multilinear products of the density,

$$\tau_l^{\text{UD}}(k) = \mathcal{Q}_N \frac{1}{2} \sum_{i, j \neq i} \hat{\mathbf{k}} \cdot \mathbf{F}_{ij} (e^{-i\mathbf{k} \cdot \mathbf{R}_i} - e^{-i\mathbf{k} \cdot \mathbf{R}_j})$$

$$\mathbf{F}_1^{\text{D}}(k) = \mathcal{Q}_N \sum_{j \neq 1} \hat{\mathbf{k}} \cdot \mathbf{F}_{1j} e^{-i\mathbf{k} \cdot \mathbf{R}_j} \quad (4.3)$$

$\mathbf{F}_{ij} = -\nabla_{\mathbf{R}_i} (U(R_{ij}) + \omega(R_{ij}))$ , and  $\Omega^\dagger$  is the one-particle irreducible Smoluchowski operator given by<sup>17,18</sup>

$$\Omega^\dagger = D \sum_{i=1}^N (\nabla_{\mathbf{R}_i} + \beta \mathbf{F}_i) \cdot \mathcal{Q}_i \nabla_{\mathbf{R}_i} \quad (4.4)$$

In eq 4.4, the projection operator  $\mathcal{Q}_i$  is defined by  $\mathcal{Q}_i B(k) = B(k) - \langle B(k) e^{-i\mathbf{k} \cdot \mathbf{R}_i} \rangle e^{-i\mathbf{k} \cdot \mathbf{R}_i}$ . The one-particle irreducible operator is obtained from<sup>17</sup>

$$\langle e^{\mathcal{O}t} \rangle_p = e^{\mathcal{Q}_N \Omega^\dagger t} \quad (4.5)$$

where  $\langle f(\mathbf{P}) \rangle_p = \int d\mathbf{P}^N f(\mathbf{P}) \Pi_m(\mathbf{P}^N)$  is the average of  $f(\mathbf{P})$  over the Maxwell distribution  $\Pi_m(\mathbf{P}^N)$ . We shall assume that the propagator  $\exp(\mathcal{Q}_N \Omega^\dagger t)$  represents the dynamics of uncorrelated binary collisions among the particles and replace  $\mathcal{Q}_N \Omega^\dagger$  by  $\Omega_2^\dagger$ , where

$$\Omega_2^\dagger = D(\nabla_{\mathbf{R}_1}^2 + \nabla_{\mathbf{R}_2}^2 + \beta \mathbf{F}_{12} \cdot (\nabla_{\mathbf{R}_1} - \nabla_{\mathbf{R}_2})) \quad (4.6)$$

is the two-particle Smoluchowski operator. Separating the two-particle Smoluchowski equation into an equation for the center of mass coordinate  $\mathbf{R} = (\mathbf{R}_1 + \mathbf{R}_2)/2$  and the relative coordinate  $\mathbf{r} = \mathbf{R}_1 - \mathbf{R}_2$ , we find that, for a hard sphere interaction, to leading order in the area fraction  $\phi = n\pi a^2$  of the spheres (of radius  $a$ ) in the suspension, the two-dimensional transport

coefficients  $\tilde{\eta}^B(k, z)/n$  and  $\tilde{\eta}_s^B(k, z)$  are given by

$$\tilde{\eta}_s^B(k, z) = 4\phi g(2a) \frac{(K_b T)^2}{4a^2} \int d\mathbf{r} d\mathbf{r}_0 \delta(r_0 - 2a) \delta(r - 2a) \tilde{A}(k, r - r_0, z) \times e^{ik/2 \cdot (\mathbf{r} - \mathbf{r}_0)} (\hat{\mathbf{k}} \cdot \hat{\mathbf{r}})(\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_0)$$

$$\tilde{\eta}^B(k, z)/n = 4\phi g(2a) \frac{(K_b T)^2}{4a^2} \int d\mathbf{r} d\mathbf{r}_0 \delta(r_0 - 2a) \delta(r - 2a) \tilde{A}(k, r - r_0, z) \times (\hat{\mathbf{k}} \cdot \hat{\mathbf{r}})(\hat{\mathbf{k}} \cdot \mathbf{r}_0) (e^{-ik/2 \cdot \mathbf{r}_0} - e^{ik/2 \cdot \mathbf{r}_0}) (e^{ik/2 \cdot \mathbf{r}} - e^{-ik/2 \cdot \mathbf{r}}) \quad (4.7)$$

where  $g(2a)$  is the pair correlation function for the suspension evaluated at the contact distance  $r = 2a$  and

$$\tilde{A}(k, r - r_0, z) = \int_0^\infty dt e^{-zt} \int d(\mathbf{R} - \mathbf{R}_0) e^{ik \cdot (\mathbf{R} - \mathbf{R}_0)} A(\mathbf{R} - \mathbf{R}_0, r - r_0, t) \quad (4.8)$$

where

$$A(\mathbf{R} - \mathbf{R}_0, r - r_0, t) = e^{\Omega_2 t} \delta(\mathbf{R} - \mathbf{R}_0) \delta(\mathbf{r} - \mathbf{r}_0) \quad (4.9)$$

For the two-dimensional system of hard spheres we find that<sup>19</sup>

$$\tilde{A}(k, r - r_0, z) = \frac{1}{4\pi D} \sum_{m=-\infty}^{\infty} e^{im(\theta - \theta_0)} K_m(\tilde{y}r^>) \left[ I_m(\tilde{y}r^<) - K_m(\tilde{y}r^<) \frac{I'_m(2a\tilde{y})}{K'_m(2a\tilde{y})} \right] \quad (4.10)$$

where  $r^> = \max\{r, r_0\}$ ,  $r^< = \min\{r, r_0\}$ ,  $\theta$  and  $\theta_0$  are the polar angles of  $\mathbf{r}$  and  $\mathbf{r}_0$  in the plane, respectively,  $\tilde{y} = (z/2D + k^2/4)^{1/2}$ , and  $I_m$  and  $K_m$  are modified Bessel functions. With this form of  $\tilde{A}(k, r - r_0, z)$ , we finally obtain

$$\tilde{\eta}_s^B(k, z) = 4\phi \tilde{\Gamma} g(2a) \sum_{l=-\infty}^{\infty} J'_l(ka)^2 \frac{K_l(y)}{-yK'_l(y)} \quad (4.11)$$

$$\tilde{\eta}^B(k, z)/n = 4\phi \tilde{\Gamma} g(2a) \sum_{l=-\infty}^{\infty} (1 + (-1)^l) J'_l(ka)^2 \frac{K_l(y)}{-yK'_l(y)}$$

where  $y = 2a\tilde{y} = (2z\tau_0 + (ka)^2)^{1/2}$  with  $\tau_0 = a^2/D$ . In the limit  $k = z = 0$ , these bare memory functions are

$$\tilde{\eta}_s^B(0, 0) = \tilde{\Gamma} 2\phi g(2a) \quad (4.12)$$

and  $\tilde{\eta}^B(0, 0) = 0$ , whereas  $\tilde{\eta}^B(k, z)/k^2$  diverges logarithmically as  $k$  and  $z$  approach zero. In the time domain the bare memory functions are given by

$$\eta_s^B(k, t) = 4\phi \tilde{\Gamma} \frac{g(2a)}{\tau_0} e^{-(ka)^2/2\tau_0} \int_0^\infty du e^{-ut/\tau_0} [J'_0(ka)^2 P_0(ka, u) + 2 \sum_{l=1}^{\infty} J'_l(ka)^2 P_l(ka, u)] \quad (4.13)$$

$$\eta(k, t)/n = 4\phi \tilde{\Gamma} \frac{g(2a)}{\tau_0} e^{-(ka)^2/2\tau_0} \int_0^\infty du e^{-ut/\tau_0} [2J'_0(ka)^2 P_0(ka, u) + 4 \sum_{l=1}^{\infty} J'_l(ka)^2 P_{2l}(ka, u)]$$

where the spectral density functions  $P_l(ka, u)$  are

$$P_l(ka, u) = \frac{1}{\pi^2 u} \frac{1}{J'_l(\sqrt{2u})^2 + N'_l(\sqrt{2u})^2} \quad (4.14)$$

and  $J_l(x)$  and  $N_l(x)$  are Bessel functions. Thus for low-density systems, in which mode coupling contributions are negligible, we find that the long time self-diffusion constant is

$$D_s(0, 0) = D_s^L = \frac{(K_b T)^2}{\tilde{\Gamma}(1 + 2\phi g(2a))} = D(1 - 2\phi g(2a) + O(\phi^2)) \quad (4.15)$$

which is the result of ref 20.

**4.2. Gaussian Approximation.** The Fourier transform of the van Hove self-correlation function  $F_s(\mathbf{R}, t)$  is often approximated<sup>23</sup> by expanding around its first cumulant such that

$$F_s(k, t) = \langle e^{-ik \cdot (\mathbf{R}_1(t) - \mathbf{R}_1(0))} \rangle = \exp\{-k^2 W(t)\} \left[ 1 + \frac{1}{2} \alpha_2(t) (k^2 W(t))^2 + O(k^6) \right] \quad (4.16)$$

where  $W(t) = \langle (\mathbf{R}_1(t) - \mathbf{R}_1(0))^2 \rangle / 4$  is the mean squared displacement and  $\alpha_2(t)$  is defined by

$$\alpha_2(t) = \frac{\langle (\Delta \mathbf{R}_1(t))^4 \rangle}{2 \langle (\Delta \mathbf{R}_1(t))^2 \rangle^2} - 1 \quad (4.17)$$

with  $\Delta \mathbf{R}_1(t) = \mathbf{R}_1(t) - \mathbf{R}_1(0)$ . Note that for two-dimensional systems in which the displacements  $\Delta \mathbf{R}_1(t)$  have a Gaussian distribution

$$\langle (\Delta \mathbf{R}_1(t))^{2n} \rangle = n! \langle (\Delta \mathbf{R}_1(t))^2 \rangle^n \quad (4.18)$$

and  $\alpha_2(t)$  vanishes. For simple liquids the first correction to the Gaussian approximation is typically 10% or less of the leading term and successive terms are even smaller.<sup>24</sup> We shall examine the quality of the Gaussian approximation for two-dimensional low-density colloid suspensions in a manner similar to that used by Cichocki and Jones<sup>25</sup> to study three-dimensional hard sphere systems.

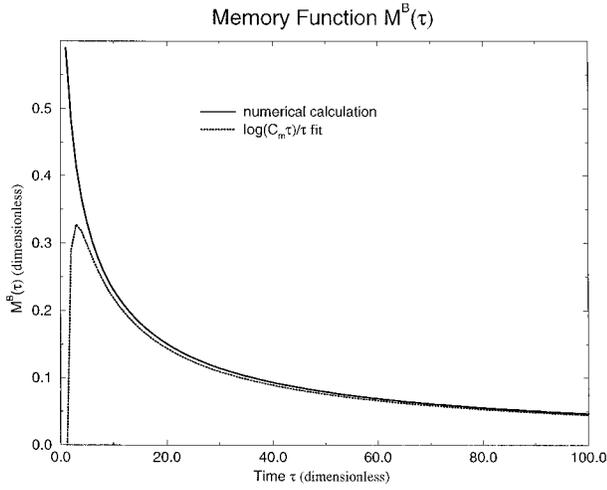
Noting that the generalized diffusion coefficient is given to leading order in the volume fraction  $\phi$  by

$$\tilde{D}_s(k, z) = D(1 - \tilde{\eta}_s^B(k, z)/\tilde{\Gamma}) \quad (4.19)$$

and that

$$\tilde{F}_s(k, z) = \frac{1}{z + \tilde{D}_s(k, z)k^2} = \frac{1}{z} - k^2 \tilde{\beta}_1(z) + k^4 \tilde{\beta}_2(z) + O(k^6) \quad (4.20)$$

by expanding  $\tilde{F}_s(k, z)$  and  $\tilde{\eta}_s^B(k, z)$  in powers of  $k$  and equating



**Figure 2.** Plot of the functions  $M^B(\tau)$  and  $\log(C_m\tau)/\tau$  versus reduced time  $\tau = t/\tau_0$ . Note how rapidly  $M^B(\tau)$  approaches its asymptotic long time form  $\log(C_m\tau)/\tau$ .

terms of the same order in  $k$ , we find

$$\tilde{\beta}_1(z) = \tilde{W}(z) = \frac{D}{z^2} (1 - \tilde{\eta}_s^{B(0)}(z)/\tilde{\Gamma}) \quad (4.21)$$

$$\tilde{\beta}_2(z) = \frac{D^2}{z^3} (1 - 2\tilde{\eta}_s^{B(0)}(z)/\tilde{\Gamma} + z\tau_0\tilde{\eta}_s^{B(2)}(z)/\tilde{\Gamma})$$

$$\tilde{\eta}_s^B(k, z) = \tilde{\eta}_s^{B(0)}(z) + (ka)^2\tilde{\eta}_s^{B(2)}(z) + O((ka)^4)$$

where  $\tau_0 = a^2/D$  and

$$\alpha_2(t) = 2\frac{\beta_2(t)}{W(t)^2} - 1 \quad (4.22)$$

From eqs 4.13 and 4.21, setting  $\tau = t/\tau_0$ ,  $W(\tau)$  and  $\alpha_2(\tau)$  are

$$W(\tau) = a^2\tau \left[ 1 - \frac{2\phi g(2a)}{\tau} \int_0^\infty dx P_s^{(0)}(x) f_1(x, \tau) \right] \quad (4.23)$$

$$\alpha_2(\tau) = \frac{4\phi g(2a)}{\tau} \int_0^\infty dx \left[ P_s^{(0)}(x) \left( f_1(x, \tau) - \frac{1}{\tau} f_2(x, \tau) \right) + \frac{1}{\tau} P_s^{(2)}(x) f_1(x, \tau) \right] + O(\phi^2)$$

where  $Dt = a^2\tau$ ,

$$P_s^{(0)}(x) = \frac{1}{\pi^2 x Z_1(\sqrt{2x})} \quad (4.24)$$

$$P_s^{(2)}(x) = \frac{1}{\pi^2 x} \left[ \frac{1}{2Z_0(\sqrt{2x})} - \frac{3}{4Z_1(\sqrt{2x})} + \frac{1}{4Z_2(\sqrt{2x})} \right]$$

$$Z_1(x) = J_1'(x)^2 + N_1'(x)^2$$

and

$$f_1(x, \tau) = \frac{1}{x^2} (e^{-x\tau} - 1 + x\tau) \quad (4.25)$$

$$f_2(x, \tau) = \frac{1}{x^3} \left[ \left( \frac{x\tau}{2} - 1 \right) (e^{-x\tau} - 1 + x\tau) + \frac{1}{2} (x\tau)^2 \right]$$

In Figure 2 we plot the memory function

$$M^B(\tau) = \frac{1}{\tau} \int_0^\infty dx P_s^{(0)}(x) \frac{(1 - e^{-x\tau})}{x^2} \quad (4.26)$$

as a function of  $\tau = t/\tau_0$  and show how rapidly it approaches its asymptotic form  $\log(\tau C_m)/\tau$ , where  $C_m = \exp\{C\}/2 \approx 0.89054$ , and  $C$  is Euler's constant. In Figure 3 we plot the function  $\alpha_2(\tau)/4\phi g(2a)$  as a function of  $\tau$  and note that the first correction to the Gaussian approximation is less than 1% of the leading term for a low-density hard sphere system. We conclude that the Gaussian approximation works extremely well in the low-density regime.

**4.3. Dense Systems.** Felderhof et al.<sup>6</sup> have suggested that the mean squared displacement  $W(t)$  in colloidal systems with repulsive potentials should be determined principally by binary uncorrelated collisions and be of the functional form

$$W(t) = D_s^L t + (D_s^S - D_s^L) \tau_L \log\left(\frac{t}{\tau_m}\right) \quad (4.27)$$

over a wide range of concentrations  $\phi$ , where  $D_s^S$ ,  $D_s^L$ ,  $\tau_L$ , and  $\tau_m$  depend on the nature of the interactions and on  $\phi$ . In this section we examine this hypothesis by applying the mode coupling formalism to calculate the parameters  $\tau_L$  and  $D_s^L$  self-consistently for a model hard disc system in which  $\tau_m = \tau_0/C_m$ . Furthermore, we test whether the mode coupling formalism, which in principle accounts for caging effects in dense fluids, yields significant deviations from the suggested functional form.

For higher densities we expect that the mode coupling terms will also contribute to the long time self-diffusion coefficient via

$$D_s^L = \frac{D}{1 + 2\phi g(2a) + \tilde{\eta}_s^{MC}(0,0)} \quad (4.28)$$

where the simple bilinear contribution to the mode coupling expression is given by

$$\tilde{\eta}_s^{MC}(0,0) = \frac{n}{2\pi} \int_0^\infty dt \int_0^{K_c} dq \frac{qh(q)^2}{1 + nh(q)} F_s(q,t) F(q,t) \quad (4.29)$$

We approximate the scattering functions  $F_s(q,t)$  and  $F(q,t)$  for self-consistent analysis using the binary collision functional forms of their memory functions,

$$F_s(q,t) = \exp\{-q^2 W(t)\}$$

$$F(q,t) = \exp\{-q^2 t D^e(q)\} \quad (4.30)$$

with

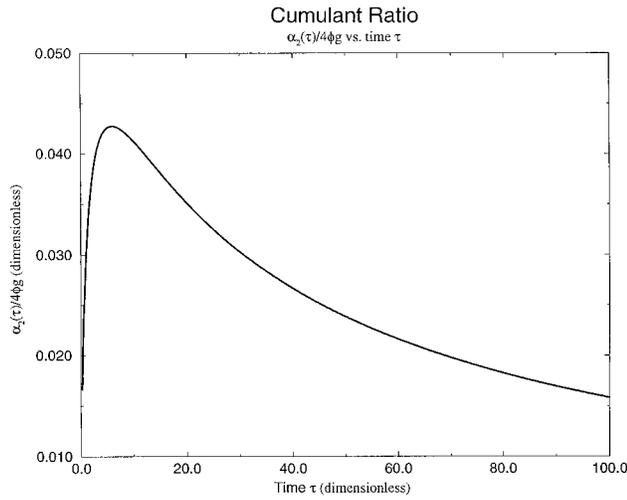
$$W(t) = \begin{cases} Dt & \text{for } Dq^2 t < 1 \\ D_s^L t + \alpha M^B(\tau)t & \text{for } Dq^2 t \geq 1 \end{cases} \quad (4.31)$$

where  $\alpha = 2\phi g(D_s^L)^2/D$  and  $M^B(\tau)$  is given by eq 4.26. In eq 4.30,  $D^e(q)$  is

$$D^e(q) = \begin{cases} \frac{D}{S(q)} & \text{for } Dq^2 t < 1 \\ \frac{D}{S(q)} \frac{1}{1 + \tilde{\eta}^B(q,0)} & \text{for } Dq^2 t \geq 1 \end{cases} \quad (4.32)$$

Note that for  $Dq^2 t < 1$  the scattering functions are approximated by their short time forms, whereas in the opposite limit the long time forms are used.

To evaluate the bilinear mode coupling contribution to the generalized friction coefficient self-consistently we use the results of Rosenfeld<sup>22</sup> for the structure factor of a two-



**Figure 3.** Plot of the ratio of the second to first cumulants  $\alpha_2(\tau)/(4\phi g)$  versus reduced time  $\tau$ .

dimensional hard disc system. Rosenfeld showed that the direct correlation functions is given by

$$-nC(k) = 4\phi \left[ A \left( \frac{J_1(ka)}{ka} \right)^2 + B J_0(ka) \frac{J_1(ka)}{ka} + G \frac{J_1(2ka)}{ka} \right] \quad (4.33)$$

with

$$\begin{aligned} \chi &= Z + \phi Z' \\ G &= (Z'/2)^{1/2} \\ A &= \frac{1}{\phi} (1 + (2\phi - 1)\chi + 2\phi G) \\ B &= \frac{1}{\phi} ((1 - \phi)\chi - 1 - 3\phi G) \end{aligned} \quad (4.34)$$

where  $Z = dz/d\phi$ . In eq 4.34,  $Z = P/nK_bT$  is the compressibility equation of state, which is well fitted by the expression

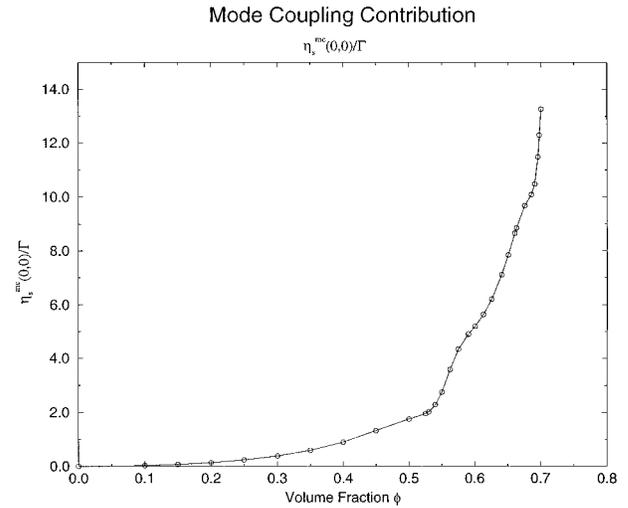
$$Z = \frac{1 + 0.128\phi^2 + 0.027\phi^3 + 0.06\phi^4}{(1 - \phi)^2} \quad (4.35)$$

It follows from these results that the pair correlation function at contact is  $g(2a) = -c(2a) = G$ . This parametrization of the two-dimensional static structure function works well for small volume fractions but underestimates the height of the first peak in  $S(k)$  for large volume fractions (around  $\phi = 0.73$ ). Furthermore, we estimate the mean distance over which a colloid particle diffuses before interacting with another particle of the system to be

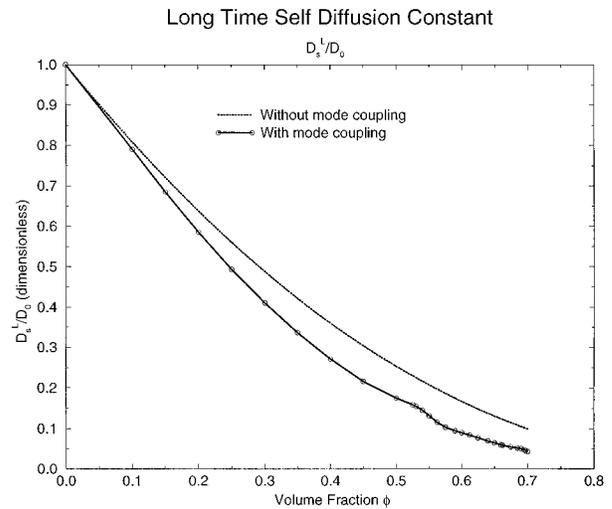
$$l \approx \frac{1}{2n^{1/2}g(2a)} \quad (4.36)$$

and therefore estimate the cutoff wavevector  $K_c$  to be  $K_c \approx 1/l = 2\sqrt{\phi}g/(a\sqrt{\pi})$ .

With these approximations it is a simple matter to evaluate  $\tilde{\eta}_s^{\text{MC}}(0,0)$  as a function of the volume fraction  $\phi$ . In Figure 4 we show  $\tilde{\eta}_s^{\text{MC}}(0,0)$  as a function of the volume fraction. At low densities the mode coupling contributions to the memory function are at least a factor of  $\phi^2$  smaller in magnitude than the binary collision contribution, and as  $\phi$  increases, the contribution of  $\tilde{\eta}_s^{\text{MC}}(0,0)$  to  $\tilde{\eta}_s(0,0)$  becomes increasingly important. In Figure 5 we plot  $D_s^L(\phi)/D$  as a function of  $\phi$  with



**Figure 4.** Plot of the dimensionless mode coupling contribution  $\tilde{\eta}_s^{\text{MC}}(0,0)/\tilde{\Gamma}$  to the long time self-diffusion coefficient  $D_s^L/D_0$  versus volume fraction  $\phi$ .



**Figure 5.** Plot of the long time reduced self-diffusion coefficient  $D_s^L/D_0$  with and without mode coupling contributions versus volume fraction  $\phi$ .

and without the bilinear mode coupling contribution. Note that at low densities  $D_s^L(\phi)/D$  is well approximated by

$$\frac{D_s^L(\phi)}{D} = \frac{1}{1 + \tilde{\eta}(0)} \approx \frac{1}{1 + 2\phi g(2a)} \quad (4.37)$$

In the asymptotic regime, where  $\sqrt{2z\tau_0} = v$  is small (i.e. for  $t \gg 2\tau_0$ ), we find that the Laplace transform of the mean squared displacement is given by

$$\begin{aligned} \tilde{W}(z) &= \frac{D}{z^2} \left( \frac{1}{1 + \tilde{\eta}_s^{(0)}(z)} \right) = \\ \frac{D_s^L}{z^2} &\left( 1 - \frac{\Delta\tilde{\eta}_s^{(0)}(z)}{1 + 2\phi g(2a) + \tilde{\eta}_s^{\text{MC}}(0,0) + \Delta\tilde{\eta}_s^{\text{MC}}(0,0) + \Delta\tilde{\eta}_s^{(0)}(z)} \right) \end{aligned} \quad (4.38)$$

where  $\Delta\tilde{\eta}_s^{(0)}(z)$  is

$$\Delta\tilde{\eta}_s^{(0)}(z) = \tilde{\eta}_s(0,z) - \tilde{\eta}_s(0,0) = \Delta\tilde{\eta}_s^{\text{B}(0)}(z) + \Delta\tilde{\eta}_s^{\text{MC}}(z) \quad (4.39)$$

It is straightforward but tedious to show that when  $t \gg \tau_0$  we have  $\tilde{\eta}(0) \gg \Delta\tilde{\eta}(z)$ , and hence the expression  $(1 + \tilde{\eta}(z))^{-1}$  can

be expanded around  $(1 + \tilde{\eta}(0))^{-1}$ , and the expression for the Laplace transform of the mean squared displacement becomes

$$\tilde{W}(z) = \frac{D}{z^2} \left( \frac{1}{1 + \tilde{\eta}(0)} - \frac{\Delta\tilde{\eta}(z)}{(1 + \tilde{\eta}(0))^2} + \frac{\Delta\tilde{\eta}(z)^2}{(1 + \tilde{\eta}(0))^3} + \dots \right) \quad (4.40)$$

At low densities  $\tilde{\eta}_{MC}(z)$  is always negligible compared to  $\tilde{\eta}^B(z)$ , but at high densities a regime where  $\tilde{\eta}^{MC}(z) \gg \tilde{\eta}^B(z)$  is reached. Explicit calculation from eq 3.27 reveals that even though  $\tilde{\eta}^{MC}(z) \gg \tilde{\eta}^B(z)$  at high densities, we still find  $\Delta\tilde{\eta}^{MC}(z) \ll \Delta\tilde{\eta}^B(z)$  for small  $z$ . Thus, despite the fact that the mode coupling effects on the memory function are pronounced, they are rapidly established on a time scale much smaller than the time scale of the binary collision contributions to the memory function. At long times the bilinear mode coupling term gives a contribution to the memory function that is bounded above in magnitude at all times by a very small  $1/\tau$  tail. This tail is much smaller than the binary collision memory terms  $M^B(t)$ . It is doubtful that the tail could ever be detected experimentally in the asymptotic long time regime. In Figure 6 we plot the effect of the mode coupling terms on the memory function  $M^{MC}(\tau)$  compared to  $M^B(\tau)$  as a function of time for several volume fractions. We conclude that the net effect of the mode coupling terms in the asymptotic long time regime is to renormalize the long time diffusion coefficient without any other significant change in the functional form of the dynamics of  $W(t)$ . Outside the long time regime we expect the mode coupling terms to alter the dynamics much more significantly.

Using eq 4.13 and Laplace inverting (4.40), we find that for  $t \gg \tau_0$  ( $\tau \equiv t/\tau_0 \gg 1$ ),  $W(t)$  is

$$W(t) = D_s^L t + \frac{2\phi g}{1 + \tilde{\eta}(0)} D_s^L t M^B(\tau) + D_s^L t \left( \frac{2\phi g}{1 + \tilde{\eta}(0)} \right)^2 M_1^B(\tau) + \dots \quad (4.41)$$

where

$$M^B(\tau) = \frac{1}{\tau} \int_0^\infty dx \frac{1 - e^{-x\tau}}{u^2} P_s^{(0)}(x)$$

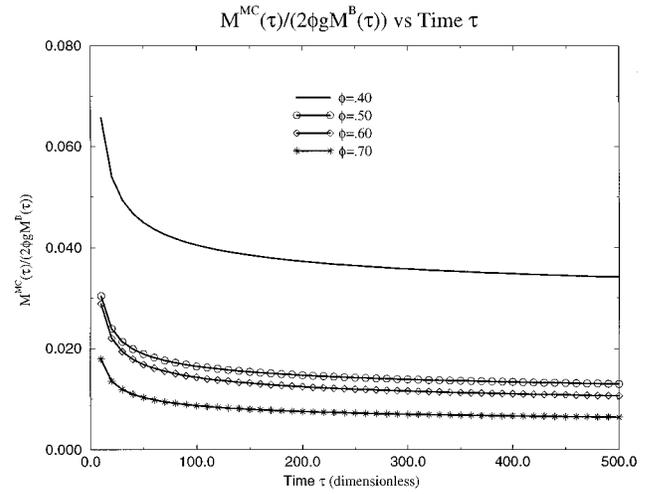
$$M_1^B(\tau) = 2M^B(\tau) + \frac{1}{\tau} \int_0^\infty dx_1 dx_2 \frac{P_s^{(0)}(x_1) P_s^{(0)}(x_2)}{x_2 - x_1} \times \left( \frac{1 - e^{-x_2\tau}}{x_2^2} - \frac{1 - e^{-x_1\tau}}{x_1^2} \right)$$

with  $P_s^{(0)}(x)$  given by eq 4.24. Numerical calculations show that  $M_1^B(\tau)$  is at least an order of magnitude smaller than  $M^B(\tau)$  when  $t \gg \tau_0$ , as shown in Figure 7.

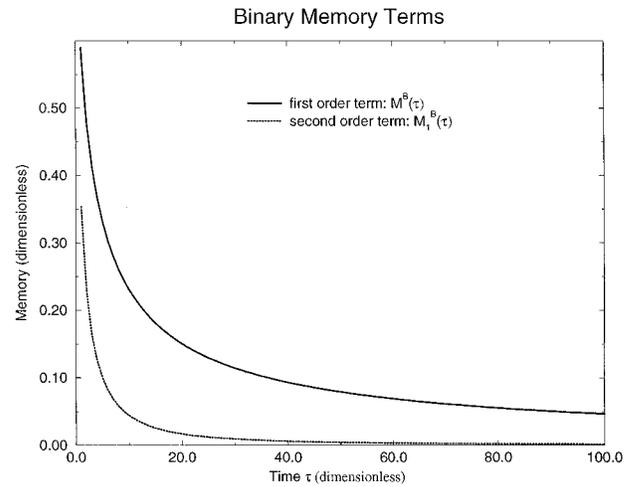
Since  $M(\tau) \approx \log(C_m \tau)/\tau$  for large  $\tau = t/\tau_0$ , we conclude that for asymptotically long times the mean squared displacement  $W(t)$  behaves approximately as

$$W(t) = D_s^L t + \frac{2\phi g}{1 + \tilde{\eta}(0)} D_s^L \tau_0 \log(C_m \tau) \quad (4.42)$$

Plotting  $W(\tau)/(C_m a^2 \tau)$  versus  $\log(C_m \tau)/(C_m \tau)$  yields a straight line whose slope and y-intercept should be  $2\phi g/(1 + \tilde{\eta}(0))^2$  and  $C_m^{-1}/(1 + \tilde{\eta}(0))$ , respectively. We therefore conclude that Felderhof's hypothesis concerning the dynamics of two-dimensional colloidal suspensions is not inconsistent with the inclusion of mode coupling effects; that is, to a good approximation the functional form of the time dependence of the mean squared displacement is not altered by mode coupling



**Figure 6.** Plot of the ratio of the contributions  $M^{MC}(\tau)/(2\phi g M^B(\tau))$  made by  $\eta_s^{MC}(\tau)$  and  $\eta_s^B(\tau)$  to the memory function versus reduced time  $\tau$  for several values of the volume fraction  $\phi$ .



**Figure 7.** Comparison of the first-order term  $M^B(\tau)$  and the second-order term  $M_1^B(\tau)$  as a function of reduced time  $\tau$ .

effects in a self-consistent treatment. It is interesting to note that the functional form of  $W(t)$  in the long time asymptotic regime does not change as a function of density even though the parameters upon which it depends,  $D_s^L$  and  $\phi$ , vary considerably.

## 5. Summary and Conclusions

In the preceding calculations we considered systems in which the colloid particles interact via a hard core potential. Cichocki and Felderhof<sup>6</sup> have investigated the effect of attractive square well interactions in addition to the hard core repulsion and have argued that the asymptotic form of the mean squared displacement for repulsive potential systems should behave as

$$W(t) = D_s^L t + (D_s^s - D_s^L) \tau_L \log(t/\tau_m) \quad (5.1)$$

in two dimensions, where the parameters  $\tau_L$  and  $\tau_m$  depend on the nature of the interactions and on the concentration  $\phi$ . Note that their expression corresponds to (4.42) with the parameters  $\tau_m = \tau_0/C_m$  and

$$\tau_L = \frac{2\phi g}{\tilde{\eta}(0)} \frac{D_s^L}{D} \tau_0 = \frac{2\phi g D_s^L}{D_s^s - D_s^L} \frac{D_s^L}{D} \tau_0 \quad (5.2)$$

We have demonstrated that the mode coupling expressions

designed to account for caging effects in dense systems do not necessarily alter the functional form of the time dependence in eq 5.1.

Our mode coupling expressions differ somewhat from those of other authors. The mode coupling expression of Medina-Noyola and co-workers<sup>16</sup> corresponds to eq 4.29 if the short time approximations are used for the scattering functions  $F_s(q,t)$  and  $F(q,t)$  in the bilinear mode coupling equation (3.7); that is, Medina-Noyola et al. set

$$\begin{aligned} F_s(k,t) &= e^{-k^2 D_0 t} \\ F(k,t) &= e^{-k^2 D_0 t / S(k)} \end{aligned} \quad (5.3)$$

which they call the ‘‘Fick plus decoupling approximation’’. This approximation scheme works well for short times and small wavevectors, where memory effects are not important, but it breaks down at long times and intermediate wavevectors, where memory effects reduce the effective diffusion coefficient and lead to slow nonexponential decay in the scattering functions. Furthermore, the mode coupling integral in the expression of Medina-Noyola and co-workers extends from zero to infinity and is not cut off at large wavevectors. Since the integrals are not cut off, they include unphysical large wavevector relaxation channels for the decay of fluctuations. This implies that the functional form used for the scattering functions does not approximate well the dynamics in the large  $q$  region. We believe that slow relaxation channels do not exist at large wavevectors since in that regime we anticipate that the generalized hydrodynamic modes no longer decay more slowly than any other ‘‘kinetic’’ modes of the system. The cutoff wavevector is a sensitive function of the density and at high densities is large enough that the range of the mode coupling integrals can effectively be extended to infinity. At low densities, however,  $K_c$  is small, which leads to small mode coupling effects.

The bilinear mode coupling contributions to the  $N$ -particle friction memory term  $\tilde{\eta}(k,z)$  exhibit more complicated behavior. For example the simple bilinear term

$$\frac{\tilde{\eta}^{\text{MC}}(k,z)}{k^2} = \int_0^{K_c} d\mathbf{q} \frac{V(k,q)}{z + (\mathbf{k} - \mathbf{q})^2 \tilde{D}^{\text{B}}(\mathbf{k} - \mathbf{q}, z) + q^2 \tilde{D}^{\text{B}}(q, z)} \quad (5.4)$$

with

$$V(k,q) = \frac{n(K_b T)^2}{4\pi^2} S(\mathbf{k} - \mathbf{q}) S(q) \left( \frac{(\mathbf{k} - \mathbf{q})C(\mathbf{k} - \mathbf{q}) + \mathbf{q}C(q)}{k} \right)^2 \quad (5.5)$$

diverges logarithmically as  $k$  and  $z$  approach zero, although  $\tilde{\eta}^{\text{MC}}(k,z)$  is well-behaved in this limit. The divergence is not surprising since it was found that  $\tilde{\eta}^{\text{B}}(k,z)/k^2$  also does not exist in the limit  $k = z = 0$ . This divergence is reminiscent of the behavior of the mode coupling contributions to the generalized transport coefficients of strictly two-dimensional fluids.<sup>7</sup> We should emphasize, however, that since  $\tilde{\eta}(k,z)$  is well-behaved for all  $k$  and  $z$ , this does not imply that the generalized diffusion coefficient  $\tilde{D}(k,z)$  does not exist for the system under consideration. In fact in the hydrodynamic limit the diffusion coefficient is simply  $D/S(k)$ .

We believe the fact that the functional form of the time dependence in eq 5.1 is determined mainly by binary uncorrelated collisions is due to the vast difference in time scales of the bath–colloid and colloid–colloid interactions. The collisions between the bath particles and a given colloid particle occur on a time scale so short that correlated collision events

among colloid particles are rarely established. In a simple hard sphere liquid a particle moves freely in a predetermined direction in between collisions, and the direction of the particle motion is strongly correlated with the motions of its neighboring particles. This correlation leads to vortex motions of the fluid. In a colloidal system, on the other hand, the numerous collisions of bath particles with a colloid particle destroy the correlation between the velocity of the colloid particle and the velocities of its neighboring colloid particles, so that only rarely is the motion of a colloid particle dependent on the motion of its neighbors.

We have restricted our attention to a simple model that assumes hydrodynamic interactions are instantaneous. Of course in real systems that they are not instantaneous, so direct comparison of our results to the dynamics of suspensions is difficult. It has been shown<sup>10</sup> that in some time regimes the hydrodynamic effects in three-dimensional suspensions cancel to a large degree, which suggests the possibility that such effects may not play an important role in determining the time dependence of  $W(t)$ . Although the conclusions we have reached for the model system seem to hold qualitatively for the physical system, any direct quantitative comparison of our results to experimental data is bound to be problematic because we have treated only the case of hard sphere interactions and instantaneous hydrodynamic effects. The only direct test of our conclusions is to compare our results with those of careful simulations that are capable of predicting the asymptotic long-time behavior of quasi two-dimensional colloid suspensions. We are not aware of any reports of numerical studies which probe this time scale regime for two-dimensional systems.

Much work remains to be done on quasi-two-dimensional colloid suspensions. We have examined only the asymptotic long time behavior of the tagged particle correlation function  $F_s(k,t)$ . At intermediate times the dynamics of  $F_s(k,t)$  in concentrated suspensions may differ significantly from the long time behavior described in this work. Outside the long time regime where  $t \approx \tau_D$ , momentum correlations play an important role in the dynamics of  $F_s(k,t)$ . Since we expect that momentum correlations persist when  $t \approx \tau_D$ , the Fokker–Planck operator rather than the Smoluchowski operator determines the time evolution of the microscopic system. Furthermore, we expect mode coupling contributions to the memory function to alter the dynamics observed in dense systems in the intermediate time regime.

Throughout this work we have assumed that long-lived collective modes exist at intermediate wavevectors ( $k \approx 1/a$ ) for colloid systems in the diffusive limit, as they do for hard sphere liquids. This assumption can be examined by an eigenvector/eigenvalue analysis of the Fokker–Planck and Smoluchowski operators to check that the extensions of the hydrodynamic modes to intermediate wavevectors are still significantly longer lived than the other ‘‘kinetic’’ modes of the system.

Many interesting questions about colloid systems can also be addressed by Brownian dynamics or other simulation techniques. One such question is of how dimensionality affects the dynamics, which could be examined by performing simulations of thin-celled systems of various thickness. Other types of potentials that include attractive parts in addition to hard cores can also be investigated.

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## References and Notes

- (1) Schaertl, W.; Sillescu, H. *J. Colloid Interface Sci.* **1993**, *155*, 313.
- (2) Marcus, A. H.; Schofield, J.; Rice, S. A. In preparation.
- (3) Marcus, A. H.; Lin, B.; Rice, S. A. *Phys. Rev. E* **1996**, *63*, 1765.
- (4) Cichocki, B.; Felderhof, B. U. *J. Chem. Phys.* **1991**, *96*, 4669.
- (5) Marcus, A. H.; Rice, S. A. Submitted to *Phys. Rev. Lett.*
- (6) Cichocki, B.; Felderhof, B. U. *J. Phys.: Condens. Matter* **1994**, *6*, 7287.
- (7) Yuan, H. H.-H.; Oppenheim, I. *Physica A* **1978**, *80*, 1; **1978**, *90*, 21.
- (8) Schofield, J.; Oppenheim, I. *Physica A* **1993**, *196*, 209.
- (9) Deutch, J. M.; Oppenheim, I. *J. Chem. Phys.* **1971**, *54*, 3547.
- (10) Tokuyama, M.; Oppenheim, I. *Phys. Rev. E* **1994**, *50*, R16.
- (11) Kamgar-Parsi, B.; Cohen, E. G. D.; de Schepper, I. M. *Phys. Rev. A* **1987**, *35*, 4781; Kirkpatrick, T. R. *Phys. Rev. A* **1985**, *32*, 3130.
- (12) de Schepper, I. M.; van Loef, J. J.; Haffmans, A. F. E. M. *J. Stat. Phys.* **1989**, *57*, 631; Kirkpatrick, T. R.; Nieuwoudt, J. C. *Phys. Rev. A* **1986**, *33*, 2651.
- (13) Schofield, J.; Lim, R.; Oppenheim, I. *Physica A* **1992**, *181*, 89.
- (14) Schofield, J.; Oppenheim, I. *Physica A* **1992**, *187*, 210.
- (15) Hess, W.; Klein, R. *Adv. Phys.* **1983**, *32*, 173.
- (16) Aranda-Espinoza, H.; Carbajal-Tinoco, M.; Urrutia-Banuendos, E.; Arauz-Lara, J. L.; Medina-Noyola, M.; Alejandre, J. *J. Chem. Phys.* **1994**, *101*, 10925.
- (17) Cichocki, B.; Hess, W. *Physica A* **1987**, *141*, 475.
- (18) Szamel, G.; Lowen, H. *Phys. Rev. A* **1991**, *44*, 8215.
- (19) Ackerson, B. J.; Fleishman, L. *J. Chem. Phys.* **1982**, *76*, 2675.
- (20) Leegwater, J. A.; Szamel, G. *Phys. Rev. A* **1992**, *46*, 4999.
- (21) Medina-Noyola, M. *Phys. Rev. Lett.* **1988**, *60*, 2705.
- (22) Rosenfeld, Y. *Phys. Rev. A* **1990**, *42*, 5978.
- (23) Nijboer, B. R. A.; Rahman, A. *Physica* **1966**, *32*, 415.
- (24) Rahman, A. *Phys. Rev.* **1964**, *136*, A405.
- (25) Cichocki, B.; Jones, R. B. *Z. Phys. B: Condens. Matter* **1987**, *68*, 513.

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