

Theory of fluctuations in colloidal suspensions undergoing steady shear flow

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The static structure factor for colloidal suspensions in systems undergoing steady shear flow is calculated using response theory in the linear regime and using a fluctuating-diffusion equation in the nonlinear regime. In the second case, the intermediate-scattering function is also obtained. The theories give the structure factor for both high and low wave vectors. In the linear regime, both methods agree, although in certain wave-vector regions, the nonlinear terms cannot be ignored. When the theory is compared to that proposed using the "Stokes" assumption, some qualitative disagreements are found. The results are discussed in light of the experiments of Clark and Ackerson [Phys. Rev. Lett. **44**, 1005 (1980)] and a possible experiment for determining the intermediate-scattering function is discussed.

I. INTRODUCTION

The behavior of systems out of equilibrium has historically been one of the main areas of interest of statistical mechanics. Lately, a number of theories which describe fluctuations about nonequilibrium states have been developed, using a variety of techniques.¹⁻¹⁸ These include the following: response theory,²⁻⁵ kinetic theory,^{2(b),9,10} and fluctuating hydrodynamics.^{6-8,11-13,15-17} By and large, the results are in agreement. Most of the studies have dealt with simple fluid systems,²⁻¹⁶ although superfluids,^{6,17} the gas-liquid interface,¹⁷ and nematic liquid crystals¹⁸ have also been examined.

Experimentally, the measurement of fluctuations in simple fluids in heat-conducting steady states was carried out by Beysens *et al.*,¹⁴ and quantitative agreement with the theoretical predictions was obtained after the latter were modified to account for finite size effects.⁷ To date, no experiments have been performed on simple fluids under shear or on the other systems mentioned above. Qualitatively, effects similar to those obtained for heat-conducting systems were predicted for molecular systems undergoing steady shear,^{3(b),4} although a number of complications make the corresponding experiment much more difficult.

Perhaps the first light scattering measurements of fluctuations in nonequilibrium systems were made by Clark and Ackerson,¹⁹ who examined aqueous colloidal suspensions of polystyrene spheres of 0.109- or 0.234- μm diam under a variety of steady-state shear flows. It is well known that these systems mimic many of the properties of single-phase molecular systems, e.g., they can form fluid or solid phases.²⁰⁻²² Moreover, they are much more readily studied owing to the large light scattering cross section of the spheres and the fact that $k\sigma \geq 1$ can be observed using light (σ denotes some characteristic interparticle distance). They interpreted their results using the "Stokes assumption" of Ashurst and Hoover.²³ This assumes that the distortion causing the shear is analogous to that induced in an elastic continuum under shear, and was

proposed in order to describe the behavior of simple fluids under high rates of shear.

In this paper, the scattering of light from colloidal suspensions undergoing simple shear is examined. It is assumed that the scattering arises solely from the colloid particles and that the densities are such that multiple scattering can be ignored. Elastic scattering measures the diagonal nonequilibrium structure factor, i.e.,

$$S_{\vec{k}} \equiv N^{-1} \langle N_{\vec{k}} N_{-\vec{k}} \rangle_{\text{ne}}, \quad (1)$$

where $N_{\vec{k}}$ is the Fourier transform of the colloid particle number density at wave vector \vec{k} , N is the number of colloid particles in the system, and $\langle \dots \rangle_{\text{ne}}$ denotes an average over the nonequilibrium ensemble. It is the calculation of this nonequilibrium correlation function which is reported in this work.

The various microscopic theories of fluctuations in molecular systems have mainly been concerned with the low wave vector or hydrodynamic regime. One exception to this was Ref. 3(b) where the static fluctuations in gases under shear and temperature gradients for \vec{k} 's larger than the inverse mean free path was examined. The main difference between this and the hydrodynamic regime was the nature of the dynamics necessary for calculating the correlations; no static correlations were considered. For the colloidal suspensions considered recently, the single-particle dynamics is roughly described by a diffusive model, albeit in the presence of strong static correlations which arise from the large, poorly screened Coulomb interaction between the colloid particles. The main source of dynamic interaction between the velocities of the various particles will be hydrodynamic in nature. Such interactions are extremely important in concentrated suspensions or in polymeric systems.²⁴ However, the strength of the hydrodynamic interactions all scale as the actual colloid packing fraction, $\phi \equiv 4\pi\rho R^3/3$, where R and ρ are the colloid radius and number density, respectively. For the systems under consideration $\phi \approx 10^{-3}$, thereby making hydrodynamic interactions negligible.

In the next section the result obtained via linear-

response theory for correlation functions out of equilibrium is used to obtain an equilibrium time correlation function expression for the structure factor in systems undergoing steady shear. Formally, this expression is identical to that obtained in Refs. 1–4. However, the nature of the dynamics is now totally different, as are the equilibrium static correlations. Two dynamical approximations are made, namely, diffusive and exponential relaxation. In the latter case, the result of the Stokes assumption used by Clark and Ackerson in interpreting their experiments is recaptured. The other ingredient is the equilibrium static structure factor. Unlike the case of simple fluids, this cannot be taken as a constant, due to the strong Coulomb interaction between the particles. A number of theories have been proposed to calculate the structure factor. The most sophisticated of these works adopt a “primitive” model for the colloid-colloid interactions, i.e., a screened Coulomb interaction, and then use integral equation²⁵ or Monte Carlo methods²⁶ to calculate the static structure factor. Alternate approaches have been considered by Ackerson,^{27(a)} who proposed a harmonic interaction model and by Medina-Noyala,^{27(b)} who used the mean spherical model for ionic mixtures.

Once the equilibrium static correlation function has been specified, the connection between the k -dependent diffusion constant and S_k in equilibrium is used to compute the nonequilibrium state structure factor. When compared with those of the Stokes assumption, similar results are obtained, with two exceptions. First, the Stokes assumption predicts a larger coupling to the shear flow at high k and, in fact, actually shows an increase in the structure seen in S_k . Second, the diffusive relaxation model shows some evidence for nonlinear behavior in the case of 0.234- μm -diam particles.

In Sec. III, a phenomenological fluctuating convective diffusive equation is used to calculate the static and dynamic structure factors in systems undergoing linear shear for arbitrary values of the shear rate. Related equations have been proposed in the study of binary mixtures under shear near the critical point²⁸ and in some theories of the non-Newtonian viscosity.²⁹ Here the system is non-critical, but still has relevant k dependence in the equilibrium static structure factor (which is nothing like the Ornstein-Zernike correlation function). Moreover, as will be discussed in Sec. II, the diffusion constant has k dependence which cannot be ignored.

While the fluctuating diffusion equation is a phenomenological approach, it has the advantage of yielding simple expressions for the nonequilibrium correlation functions. Moreover, the expression reduces exactly to that obtained by the diffusive relaxation model in Sec. II, as should happen if the approach is to be believed. In addition, it is easy to derive expressions for the quadratic shear rate correction to the static structures factor, as well as the asymptotic behavior for infinite shear rate. As is shown in this section, convection results in a nonexponential relaxation at sufficiently high shear rates. Unfortunately, this same convection complicates the experiment needed to measure the intermediate-scattering function. A possible experimental configuration is suggested which overcomes these problems. The case which gave the larg-

est nonlinear effects in Sec. II is reexamined and a large change in the structure factor in the vicinity of the first maximum is found. Section IV contains a summary and discussion of the main points of this work.

II. LINEAR RESPONSE: DIFFUSION AND STOKES ASSUMPTION

In Refs. 1–4, linear-response theory for systems undergoing shear was used to show that

$$S_{\vec{k}} = S_k^{(0)} - \beta N^{-1} \int_0^\infty dt \langle N_{\vec{k}}(t) N_{-\vec{k}}(t) \vec{\tau}_T \rangle : \vec{\nabla} \vec{v}(\vec{r}), \quad (2)$$

where $S_k^{(0)}$ is the equilibrium structure factor, $\beta = 1/k_B T$, $\langle \dots \rangle$ denotes an equilibrium average, $\vec{\tau}_T$ is the volume integral of the stress tensor, and $\vec{v}(\vec{r})$ is the fluid velocity field at position \vec{r} . Equation (2) is valid to linear order in velocity gradients and assumes that $\vec{\nabla} \cdot \vec{v} = 0$. Even without knowing the precise form of the time correlation function appearing in the integrand in Eq. (2), it is clear that as $k \rightarrow 0$ its decay time will become infinite, since the total number of colloid particles is a constant of the motion. Moreover, it is reasonable that the collective colloid particle motion will, to a large extent, be diffusive in nature. Thus it is assumed, at least for the purposes of computing the slowest decaying part of the time correlation function in Eq. (2), that

$$N_{\vec{k}}(t) \approx e^{-D_k k^2 t} N_{\vec{k}}(0), \quad (3)$$

where D_k is a generalized diffusion constant (e.g., as would be measured from the width of the central peak in an equilibrium inelastic scattering experiment).

Equation (3) allows Eq. (2) to be rewritten as

$$S_{\vec{k}} = S_k^{(0)} - \frac{\beta N^{-1}}{2D_k k^2} \langle N_{\vec{k}} N_{-\vec{k}} \vec{\tau}_T \rangle : \vec{\nabla} \vec{v}(\vec{r}). \quad (4)$$

The equilibrium equal-time average can be readily computed by noting that

$$\vec{\tau}_T = \frac{d}{dt} \sum_j \vec{r}_j \vec{p}_j, \quad (5)$$

where \vec{r}_j and \vec{p}_j denote the position and momentum of the j th particle, respectively (note that the sum includes both colloid and fluid particles). Inserting Eq. (5) into the average on the right-hand side of Eq. (4), using stationarity to move the time derivative to the factors of colloid density and evaluating the resulting average, yields

$$s_{\vec{k}} = S_k^{(0)} + \frac{1}{k} \frac{\partial S_k^{(0)}}{\partial k} \frac{\hat{k} \hat{k} : \vec{\nabla} \vec{v}}{2D_k}, \quad (6)$$

where \hat{k} denotes a unit vector in the \vec{k} direction. In obtaining this last result the equilibrium system was taken to be isotropic. Note that though the expression explicitly contains a factor of $1/k$, no divergence is present since the derivative of the static structure factor vanishes as k when $k \rightarrow 0$.

At first sight, it might seem that the diffusion constant would be k independent and could be set equal to its $k=0$ value (i.e., the macroscopic diffusion constant) in the light

scattering regime. However, this is *not* the case in systems where the colloid particles are strongly interacting,^{22,27} as they are in the low ionic strength considered by Clark and Ackerson. There are intercolloid static correlations which are important at not too high wave vectors; these will modify the *collective* diffusion constant, even if the individual colloid-particle velocity relaxations are uncoupled. That this indeed takes place, has been shown in the experiments of Brown *et al.*²² on dilute suspensions of latex spheres. They find that

$$D_k \approx \frac{D_s}{S_k^{(0)}}, \quad (7)$$

this also being the conclusion of a number of theoretical works.^{27,30-32} In Eq. (7), D_s is the self-diffusion constant for a single sphere and can be approximated (up to poorly understood^{27,33} factors of 2-3) by the Stokes-Einstein relation; $D_s = k_B T / 6\pi\eta R$, where η and R are the solvent viscosity and colloid-particle radius, respectively. The role of mode coupling in the diffusion process has been considered by Harris,³² who finds it to be small. Using the k -dependent diffusion constant given by Eq. (7) in Eq. (6) allows the latter to be rewritten as

$$S_{\vec{k}} = S_k^{(0)} \left[1 + \frac{\hat{k}\hat{k}:\vec{\nabla}\vec{\nabla}}{2kD_s} \frac{\partial S_k^{(0)}}{\partial k} \right]. \quad (8)$$

The static correlations between the colloid particles are complicated by uncertainties in their degree of ionization, the effective screening length, and by the fact that most experiments have been carried out close to the "freezing" point (i.e., where the colloid forms a lattice). Nonetheless, based on the work of Verwey and Overbeek,³⁴ it is generally assumed that the interaction potential between the colloid particles is pairwise additive and of the form

$$U(r) = \begin{cases} \infty, & r < 2R \\ \frac{\phi^2 \epsilon R^2}{r} \exp[-\lambda(r-2R)], & r \geq 2R \end{cases} \quad (9)$$

where λ , ϵ , and ϕ are the inverse screening length, fluid dielectric constant, and colloid surface potential, respectively. For the systems under consideration, various estimates²² give $\lambda \approx 3000 \text{ \AA}$ and $\phi \approx 100-300 \text{ mV}$. Given Eq. (9), there is still the task of calculating $S_k^{(0)}$. A number of approximations suggest themselves, namely the hypernetted chain (HNC) and Percus-Yevick (PY). Shafer²⁶ has shown that the HNC approximation yields a much better fit to experiment, at least for the small particles considered in Ref. 22. The HNC equation, in conjunction with Eq. (9), was solved numerically using the method described in Ref. 35 and $S_k^{(0)}$ and its first derivative were tabulated.

For the remainder of this work, it is assumed that the system is undergoing linear shear, with $\vec{v}(\vec{r}) \equiv \hat{y}x\omega_0$. In this case, the maximum value of $\hat{k}\hat{k}:\vec{\nabla}\vec{\nabla}$ is $\frac{1}{2}$ and is attained when $\vec{k} \propto (1,1,0)$. In Figs. 1 and 2, the prediction of Eq. (8) is shown along the direction of maximum distortion using HNC static structure factors. The values for the surface potential and screening length should only be

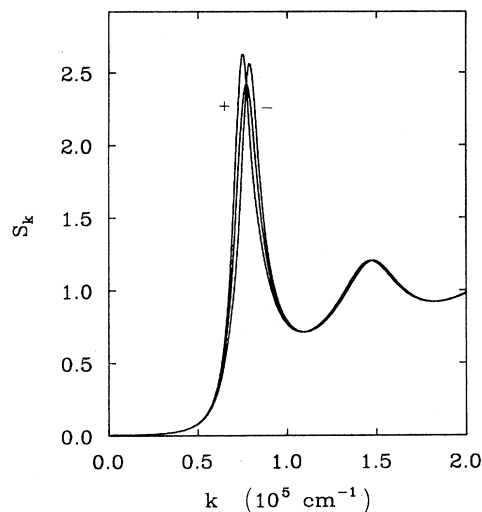


FIG. 1. S_k for a suspension of $1.40 \times 10^{12}/\text{cm}^3$, $0.109 \mu\text{m}$ -diam particles in water at 20°C using Eq. (8). The surface potential $\Phi = 115 \text{ mV}$ and $\lambda^{-1} = 3050 \text{ \AA}$. The curves correspond to shear rates $\omega_0 = 0.0, 15.0 \text{ sec}^{-1}$, labeled (+) and -15.0 sec^{-1} , labeled (-).

considered as representative. No fit to experiment was possible since detailed measurements of $S_k^{(0)}$ were not reported in Ref. 19. Note that most of the effect is for low wave vectors. At higher k the diffusion relaxation time is too fast and the coupling to the ($k=0$) linear shear vanishes. Also note the significant dip in the $-\omega_0$ curve in Fig. 2 just before the first peak. In fact, by increasing the shear rate the structure factor predicted by Eq. (8) will become negative in this region. This is due to the breakdown of the linearization implicit in Eq. (8). Before discussing the nonlinear theory, the connection to the Stokes assumption used by Clark and Ackerson in analyzing their experiment is examined.

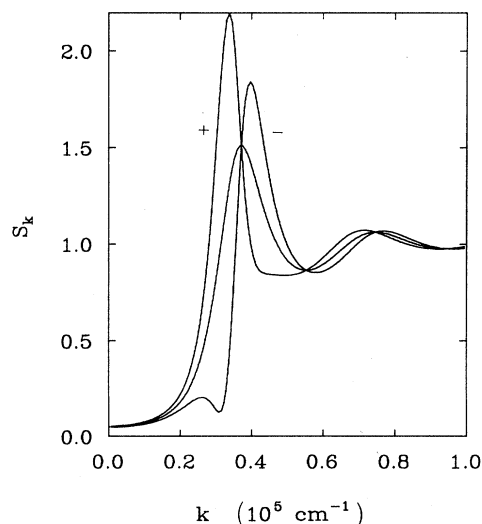


FIG. 2. S_k for a suspension of $1.42 \times 10^{11}/\text{cm}^3$, $0.234\text{-}\mu\text{m}$ -diam particles in water using Eq. (8). The remaining parameters are as in Fig. 1.

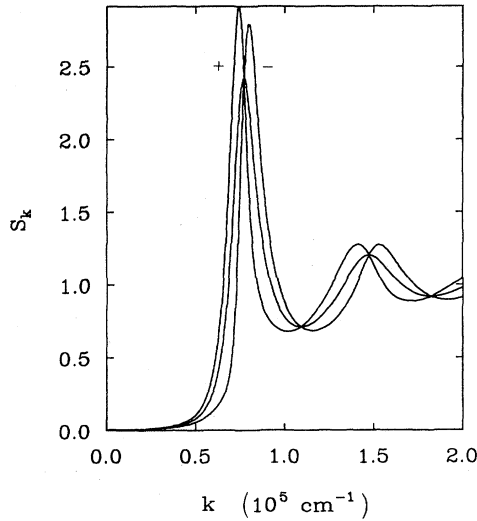


FIG. 3. Same as Fig. 1 but now using Eq. (10) with $\tau_a = 0.008$ sec.

The result of the Stokes assumption can be derived from Eq. (2) by assuming that the integrand decays exponentially with decay time τ_a . Comparing with Eq. (8) gives the following correspondence:

$$\tau_a \Leftrightarrow \frac{1}{2} D_k k^2 = S_k^{(0)} / (2D_s k^2). \quad (10)$$

The Stokes assumption yields a qualitatively different prediction, as is shown in Figs. 3 and 4. Note the persistence of the shear coupling to much higher k 's. In fact, there is an enhancement of the structure at high k . This implies that the imposition of a shear flow might cause higher-order Debye-Scherrer rings to become visible.

Physically, this arises from the fact that in the Stokes model the relaxation of density fluctuations at all length scales occurs at the same rate, e.g., as is the case in solids. On the other hand, in the diffusive picture, very short

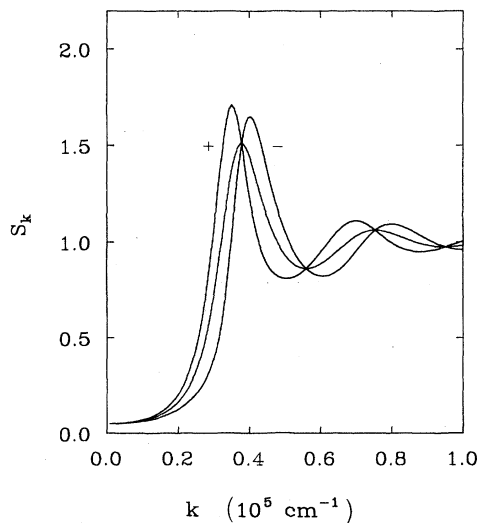


FIG. 4. Same as Fig. 2 but now using Eq. (10) with $\tau_a = 0.013$ sec.

wavelength phenomena relax much faster than those of longer wavelength. The experiments of Brown *et al.*²² support this, although to be fair, they considered much smaller particles. Moreover, the assumptions leading to Eq. (7) in no way negate the fact that the basic process is diffusive in nature, to be sure, in a system with strong initial correlations.

III. NONLINEAR BEHAVIOR: DYNAMIC AND STATIC STRUCTURE FACTORS

While the expression given by Eq. (8) rests on somewhat more microscopic foundations than the Stokes assumption, it is clear, at least in the case of Fig. 2, that it is starting to break down in the low- k region. There are three possible reasons for this: The diffusion assumption for the relaxation [i.e., Eq. (3)] is incorrect, the assumed form for D_k is not valid in some wave-vector regimes, or nonlinear effects are becoming important. In order to examine the nonlinear domain, a fluctuating convective diffusion model is now used to construct the correlation functions. Although this is a phenomenological approach, it has the advantage of yielding both the dynamic and static structure factors when the shear rate is large. Moreover, as will be shown below, the two methods agree in the linear regime. In the fluctuating diffusion equation model, it is assumed that the fluctuations obey the macroscopic equation of motion, linearized about the steady state. A random diffusion current is added to the equation in order to include all the short time and length scale processes not adequately described by the macroscopic equation. Thus for the case of linear shear,

$$(i\omega + k^2 D_k) N(\vec{k}, \omega) = \omega_0 k_y \frac{\partial N(\vec{k}, \omega)}{\partial k_x} + i \vec{k} \cdot \vec{\Gamma}_{\vec{k}, \omega}, \quad (11)$$

where a time Fourier transform has been introduced. The random diffusion current will be taken to be a white-noise process with correlation given by the Einstein relation

$$N^{-1} \langle \vec{\Gamma}_{\vec{k}, \omega} \vec{\Gamma}_{\vec{k}', \omega'}^\dagger \rangle \equiv (2\pi)^4 \delta(\vec{k} - \vec{k}') \delta(\omega - \omega') 2D_k S_k^{(0)}, \quad (12)$$

where the dagger denotes Hermitian conjugation. Equation (12) is the usual result for the random current correlations. Since the random currents represent fast, short-wavelength processes, it is reasonable to assume that Eq. (12) holds locally in steady state.

Equation (11) is easily solved, subject to the boundary condition that $N(\vec{k}, \omega)$ remain bounded as $\vec{k}_x \rightarrow \pm \infty$. The result is

$$N(\vec{k}, \omega) = \int_{k_x}^{\pm \infty} \frac{d\tilde{k}_x}{|\omega_0 k_y|} e^{[\Phi(\vec{k}, \omega) - \Phi(\tilde{k}, \omega)]} i \tilde{k} \cdot \vec{\Gamma}_{\tilde{k}, \omega}, \quad (13)$$

where

$$\Phi(\vec{k}, \omega) \equiv \left[i\omega k_x + \int^{k_x} d\tilde{k}_x (\tilde{k}_x^2 + \vec{k}_\parallel^2) D(\tilde{k}_x, \vec{k}_\parallel) \right] / (k_y \omega_0)$$

and

$$\vec{k}_{||} = (0, k_y, k_z).$$

The upper (lower) sign in Eq. (13) should be used when $\omega_0 k_y$ is positive (negative). The correlation function is easily obtained using Eqs. (12) and (13). The result is

$$\begin{aligned} & N^{-1} \langle N(\vec{k}, \omega) N^\dagger(\vec{k}', \omega') \rangle \\ &= (2\pi)^4 \delta(\omega - \omega') \delta(\vec{k}_{||} - \vec{k}'_{||}) \\ & \times \int_{\omega_0 k_y, \max(k_x, k'_x)/|k_y \omega_0|}^{\infty} d\tilde{k}_x \frac{(\tilde{k}_x^2 + k_{||}^2) D_{\vec{k}} S_{\vec{k}}^{(0)}}{(\omega_0 k_y)^2} \\ & \times \exp \left[\frac{i\omega(k_x - k'_x)}{\omega_0 k_y} - \frac{1}{|\omega_0 k_y|} \right. \\ & \left. \times \left[\int_{k_x k_y \omega_0 / |k_y \omega_0|}^{\tilde{k}_x} dk_1 (k_1^2 + k_{||}^2) D_{\vec{k}_1} + \int_{k'_x k_y \omega_0 / |k_y \omega_0|}^{\tilde{k}_x} dk_1 (k_1^2 + k_{||}^2) D_{\vec{k}_1} \right] \right]. \end{aligned} \quad (14)$$

It is more convenient to carry out the analysis of Eq. (14) in the time domain. (Note that for typical diffusion time scales, scattering experiments use an autocorrelator and thus measure the time correlation function directly.) Inverting the time Fourier transform in Eq. (14) gives

$$N^{-1} \langle N_{\vec{k}}(t) N_{\vec{k}}^\dagger(0) \rangle = (2\pi)^3 \delta(\vec{k}_{||} - \vec{k}'_{||}) \delta(k_x + \omega_0 k_y t - k'_x) F(\vec{k}; t), \quad (15)$$

where the intermediate-scattering function is defined by

$$\begin{aligned} F(\vec{k}; t) \equiv & \int_{\omega_0 k_y, \max(k_x, k_x + \omega_0 k_y t)/|k_y \omega_0|}^{\infty} d\tilde{k}_x \frac{(\tilde{k}_x^2 + k_{||}^2) 2D_{\vec{k}} S_{\vec{k}}^{(0)}}{|\omega_0 k_y|} \\ & \times \exp \left[-\frac{1}{|\omega_0 k_y|} \left[\int_{k_x k_y \omega_0 / |\omega_0 k_y|}^{\tilde{k}_x} dk_1 (k_1^2 + k_{||}^2) D_{\vec{k}_1} \right. \right. \\ & \left. \left. + \int_{(k_x + k_y \omega_0 t) k_y \omega_0 / |\omega_0 k_y|}^{\tilde{k}_x} dk_1 (k_1^2 + k_{||}^2) D_{\vec{k}_1} \right] \right]. \end{aligned} \quad (16)$$

The fact that D_k and $S_k^{(0)}$ depend only on the magnitude of \vec{k} implies that $F(\vec{k}, t)$ is even under $\vec{k} \rightarrow -\vec{k}$ simultaneously changing t to $-t$. Note, that while Eq. (14) would still be valid if D_k were allowed to be frequency dependent, the Fourier transform could not be inverted as easily; thus Eq. (16) is restricted to frequency-independent diffusion processes.

The role of the shear flow in distorting the correlation can be seen more clearly by rewriting Eq. (16) as

$$F(\vec{k}, t) = \exp \left[- \int_{k_x}^{k_x + \omega_0 k_y t} \frac{dk_1}{\omega_0 k_y} (k_1^2 + k_{||}^2) D(k_1, \vec{k}_{||}) \right] S(k_x + k_y \omega_0 t, \vec{k}_{||}), \quad \omega_0 k_y > 0, \quad t > 0 \quad (17a)$$

$$= \exp \left[- \int_{k_x + \omega_0 k_y t}^{k_x} \frac{dk_1}{\omega_0 k_y} (k_1^2 + k_{||}^2) D(k_1, \vec{k}_{||}) \right] S(k_x, \vec{k}_{||}), \quad \omega_0 k_y > 0, \quad t < 0. \quad (17b)$$

The behavior for $\omega_0 k_y < 0$ can be obtained by letting $(\vec{k}, t) \rightarrow (-\vec{k}, -t)$ in Eqs. (17). The exponential prefactors in Eq. (17) describe the loss of correlation due to diffusion. [In fact, as $\omega_0 \rightarrow 0$, they become equal to $\exp(-D_k k^2 |t|)$ as expected.] Equation (17a) is exactly what the Onsager regression hypothesis would predict for the time correlation function, although it must be stressed that the static structure factor is very different from that

given by the local equilibrium assumption. For long times, the decay given by Eqs. (17a) and (17b) will not be exponential. Consider Eq. (17a). By neglecting the k dependence of D_k , the exponential becomes

$$\exp\{-D_s k^2 t [1 + k_x k_y \omega_0 t + (\omega_0 k_y t)^2 / 3]\},$$

which, in the long-time or high-shear-rate limits, is dominated by the t^3 factor in the exponent.

The factor of $\delta(k_x + \omega_0 k_y t - k'_x)$ is caused by the distortion of the correlation by the colloid particles moving along the shear streamlines and unfortunately complicates the analysis of the dynamic scattering experiment; in the limit of high shear rate, the details of the incident beam profile cannot be ignored. Consider the autocorrelated scattered intensity at momentum transfers \vec{k} , $I(\vec{k}, t)$, as measured in a heterodyne experiment. By assuming geometric optics for the incident beam and quasielastic scattering, $I(\vec{k}, t)$ can be written as

$$I(\vec{k}, t) \propto \iint d\vec{r}_1 d\vec{r}_2 e^{i\vec{k} \cdot (\vec{r}_1 - \vec{r}_2)} E(\vec{r}_1) E^*(\vec{r}_2) \times \langle N(\vec{r}_1, t) N(\vec{r}_2, 0) \rangle, \quad (18)$$

where the incident electric field is $\text{Re}[E(\vec{r}) e^{-i\vec{k}_{\text{inc}} \cdot \vec{r}}]$ (\vec{k}_{inc} is the incident wave vector) and the asterisk denotes complex conjugation. By introducing Fourier transforms and the intermediate-scattering function, Eq. (18) can be rewritten as

$$I(\vec{k}, t) \propto \int \frac{d\vec{k}'}{(2\pi)^3} E(\vec{k} - \vec{k}') \times E^*(\vec{k} - \vec{k}' - \vec{e}_1 \omega_0 k'_y t) F(\vec{k}', t), \quad (19)$$

where

$$E(\vec{k}) \equiv \int d\vec{r} e^{i\vec{k} \cdot \vec{r}} E(\vec{r})$$

and \vec{e}_1 is the unit vector in the x direction. Clearly, the more the incident beam is like a plane wave, the more the observed time dependence will be governed by the details of $E(\vec{k})$. Let d be a typical incident beam dimension in the x direction. The width of the dispersion in the incident beam can be estimated by $d\Delta k \approx 2\pi$. In addition, $F(\vec{k}, t)$ is expected to decay on the $(D_s k^2)^{-1}$ time scale. Hence, the condition that the observed time decay be given by F and not the details of E is $\omega_0 k_y d / (D_s k^2) < 1$. For the conditions of Fig. 2 (i.e., $D_s = 1.8 \times 10^{-8}$ cm²/sec and $k = 4 \times 10^4$ cm⁻¹), a typical beam dimension of 0.01 cm implies that $\omega_0 < 10$ sec⁻¹.

Some experimental aspects of the high shear limit can be seen by modeling the incident beam by a plane wave in the y and z directions and having a Gaussian profile in the x direction, i.e.,

$$E(\vec{k}) \propto e^{(k_x d)^2/2} \delta(-\vec{k}_{\parallel}). \quad (20)$$

Using Eq. (20) in (19) gives

$$I(\vec{k}, t) \propto e^{-(k_y d \omega_0 t / 2)^2} \times \int d\Delta k e^{-(d\Delta k)^2} F(k_x - \frac{1}{2}k_y \omega_0 t + \Delta k, \vec{k}_{\parallel}; t), \quad (21)$$

which, in the limit of large d , can be approximated by

$$I(\vec{k}, t) \propto e^{-(k_y d \omega_0 t / 2)^2} F(k_x - \frac{1}{2}k_y \omega_0 t, \vec{k}_{\parallel}; t). \quad (22)$$

From Eq. (16), it follows that $F(k_x - \frac{1}{2}k_y \omega_0 t, \vec{k}_{\parallel}; t)$ is an even function of t . Thus in the high shear limit, at least for a Gaussian profile, the time correlation has a Gaussian decay, essentially determined by the incident beam.

A way in which the experimental problems associated with $\delta(k_x + \omega_0 k_y t - k'_x)$ might be overcome is by using a two-beam experiment. That is, heterodyne two-scattered beams into separate detectors and cross correlate the outputs. Such a configuration would result in the measurement of $F(\vec{k}; t)$ for $t \approx -(k_x - k'_x) / (\omega_0 k_y)$, where k_x and k'_x are the x components of the momentum transfers in the two scattered beams. Of course, the two scattering directions must still be chosen to give the same momentum transfers in the y and z directions. Some further discussion of the two-beam scattering experiment is found in Ref. 16, although there, the nature of the system's correlations gave a result which rapidly decreased as $k_x - k'_x$ was increased. This is not the case here. Two-beam measurements on colloidal suspensions have been performed recently in Ref. 20(b).

From the preceding discussion, it is clear that the quantity most amenable to theoretical and experimental analysis is the static structure factor. A number of general properties of $S_{\vec{k}}$ can be deduced from Eq. (16) without knowing the precise details of $S_{\vec{k}}^{(0)}$ or $D_{\vec{k}}$. First, should $S_{\vec{k}}^{(0)}$ be independent of k for the wave vectors of interest, then all the integrals can be carried out, with the result that $S_{\vec{k}} = S^{(0)}$ for all ω_0 . Second, in the limit of vanishing shear rate,

$$S_{\vec{k}} \approx S_{\vec{k}}^{(0)} + \frac{\omega_0 \hat{k}_x \hat{k}_y}{2k D_{\vec{k}}} \frac{\partial S_{\vec{k}}^{(0)}}{\partial k} + \frac{(\omega_0 \hat{k}_y)^2}{4D_{\vec{k}}} \frac{\partial}{\partial k_x} \left[\frac{k_x}{D_{\vec{k}} k^3} \frac{\partial S_{\vec{k}}^{(0)}}{\partial k} \right] + O(\omega_0^3). \quad (23)$$

The linear term is *exactly* what was obtained using linear-response theory [cf. Eqs. (6) and (8)]. The quadratic term is new. Clearly it cannot be ignored near the extrema of $S_{\vec{k}}^{(0)}$ or for certain scattering directions. For example, the linear term vanishes when $k_x = 0$ and

$$S_{\vec{k}} \approx S_{\vec{k}}^{(0)} + \left[\frac{\omega_0 \hat{k}_y}{2D_{\vec{k}} k^2} \right]^2 k \frac{\partial S_{\vec{k}}^{(0)}}{\partial k} + O(\omega_0^3). \quad (24)$$

Finally, in the limit of infinite shear rate (ignoring the possibility of turbulence), Eq. (16) becomes

$$S_{\vec{k}} \approx 1 - \frac{2}{|\omega_0 k_y|} \times \int_{k_x k_y \omega_0 / |k_y \omega_0|}^{\infty} d\tilde{k}_x (\tilde{k}_x^2 + k_{\parallel}^2) D(\tilde{k}_x, k_{\parallel}) \times [S^{(0)}(\tilde{k}_x, k_{\parallel}) - 1] + O(\omega_0^{-2}). \quad (25)$$

The fact that $S_{\vec{k}}^{(0)} \rightarrow 1$ as $k \rightarrow \infty$ was used in obtaining this last result. This is totally different behavior from either

of the linear predictions [i.e., Eqs. (8) and (10)]. Equation (25) implies that in the limit of very high shear, any structure in $S_{\vec{k}}$ disappears. Of course, the shear rate might be so large that Eq. (11) breaks down. This result should not be too surprising in light of the fact that shear flows were used by Clark and Ackerson^{20(a)} to prevent colloidal suspensions from ordering. Note that the ranges of validity of the asymptotic expansions given in Eqs. (23)–(25) depend on k , since the expansion parameter in Eqs. (23) and (25) is roughly $\omega_0/(k^2 D_k)$. This implies, providing D_k has not become too large due to the smallness of $S_{\vec{k}}^{(0)}$,

that the low-wave-vector regimes will exhibit larger nonlinear effects than high ones. Since the degree of nonlinearity is wave vector dependent, different experiments could lead to different conclusions concerning the linearity of the phenomena, i.e., the results will depend on precisely which wave vectors are being observed. For the system considered in Fig. 2, a shear rate of 15 sec^{-1} implies that a transition from linear to nonlinear behavior occurs at $k \approx 3 \times 10^4 \text{ cm}^{-1}$, i.e., right in the vicinity of the first Debye-Scherrer peak.

Using Eqs. (7) and (16), $S_{\vec{k}}$ can be written as

$$S_{\vec{k}} = \frac{2D_s}{|k_y \omega_0|} \int_{k_x k_y \omega_0 / |k_y \omega_0|}^{\infty} d\tilde{k}_x (\tilde{k}_x^2 + k_{\parallel}^2) \exp \left[-\frac{2D_s}{|k_y \omega_0|} \int_{k_x k_y \omega_0 / |k_y \omega_0|}^{\tilde{k}_x} dx \frac{(x^2 + k_{\parallel}^2)}{S^{(0)}(x, k_{\parallel})} \right]. \quad (26)$$

The static structure factor is plotted in Fig. 5 for the same conditions as Fig. 2. The result is quite different. The dip preceding the first maximum has completely disappeared. On the other hand, the maximum values attained by $S_{\vec{k}}$ are now less than the equilibrium maximum and the peaks are somewhat broader. This should not be too surprising since [cf. Eq. (23)] it is clear that the linear theory will always break down in the vicinity of the extrema of $S_{\vec{k}}$. In addition, note that the linear theory is becoming more accurate at high k 's.

IV. SUMMARY AND CONCLUSIONS

In this work, a detailed theory for the dynamic and static correlations in colloidal systems undergoing shear

flow has been presented. This yielded theoretical predictions for the high- and low-wave-vector correlation functions which complement those obtained in Ref. 3(b). The colloidal systems exhibit strong static correlations and relatively simple dynamics. While this is clearly one aspect of the situation in molecular liquids, it is obvious that the high- k dynamics is also going to be modified in some nontrivial way, although the recent works of de Schepper and Cohen³⁶ on the high- k equilibrium dynamic structure factor of low-density liquids indicates that collective modes still play a key role.

As was discussed in the preceding section, the linear theory will not be valid over all wave vectors; it breaks down at low wave vectors or near the extrema of $S_{\vec{k}}$. Note that k is still large enough such that wall effects should be negligible. In addition, the behavior at high rates of shear resulted in a loss of correlation, asymptotically yielding the ideal gas result. Finally note that the nonlinear terms do not have the simple angular dependence predicted by the factor of $\hat{k}\hat{k}:\vec{v}\vec{v}$, cf. Eq. (8) and this can be used to facilitate their detection.

As well as causing some interesting nonlinear effects in the static structure factor, there are nonlinear effects in the intermediate-scattering function as well; notably, the decay of $F(\vec{k};t)$ becomes nonexponential at high shear rate and a time-dependent factor of $\delta(k_x + \omega_0 k_y t - k'_x)$ appears. It is this last factor which complicates the measurement of the intermediate-scattering function, although the two-beam configuration described in the preceding section should circumvent the problem. It should be noted that the nonexponential time dependence implies that a shear-dependent diffusion coefficient not be defined for this problem, as it could in the case of the non-Newtonian viscosity calculations cited in the Introduction.

Finally, it must be stressed that the theory need not have any adjustable parameters. The only input is the forms of the equilibrium structure factor and diffusion constant. Clearly what is needed is a detailed measurement of $S_{\vec{k}}$ in and out of equilibrium and an equilibrium measurement of D_k . These must be performed above the colloid freezing temperature.

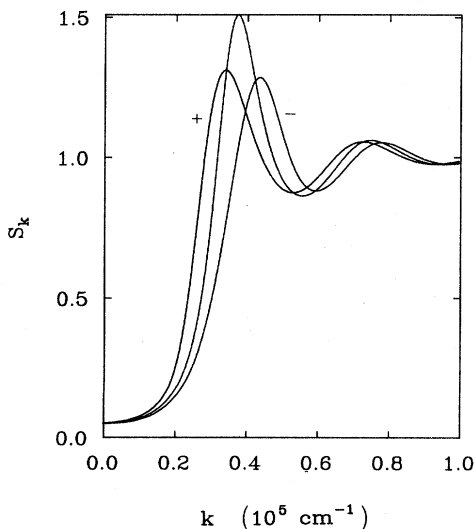


FIG. 5. Same as Fig. 2 but now using the nonlinear form for the static structure factor given by Eq. (26).

Note added in proof. Some recent work of Hanley *et al.*³⁷ based on the nonequilibrium molecular dynamics study of soft sphere fluids under shear by Hess and Hanley³⁸ indicate some interesting features in the Debye-Scherrer ring patterns (specifically "spiral nebulae"). The nonlinear theory presented in Sec. III is currently being applied to this case and the results will be reported in the near future.

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