Comparison of small shear flow rate–small wave vector static structure factor data with theory

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Comparison of small shear flow rate–small wave vector static structure factor data with theory

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Light scattering measurements determined the ratio of the nonequilibrium to equilibrium static structure factor for suspensions of "hard spheres" undergoing shear flow as a function of volume fraction of the suspended particles, the shear rate, and a limited number of scattering angles. These data are compared with existing theoretical predictions for the static structure factor ratio in the limit of small shear flow rates. We conclude that the existing theories, some which are considered exact at low volume fractions, give increasingly poor estimates of the true structure factor at small scattering angles as the volume fraction increases.

I. INTRODUCTION AND BACKGROUND

One of the primary goals of colloid science is to understand macroscopic properties of suspensions in terms of solvent and particle properties. The interparticle order plays an important role in influencing suspension properties, as many properties may be related to weighted integrals of the two particle correlation function.[1] For this reason the equilibrium two particle correlation function has been studied experimentally by measuring the static structure factor in scattering experiments using light, x rays or neutrons.[2] Because equilibrium properties do not depend on system dynamics but only on the interparticle potential, results developed to understand the two particle correlation function in pure atomic systems have also been applied directly to colloidal systems.[3,4] This analogy between atomic and colloidal systems has proved fruitful.

Nonequilibrium properties of suspensions may also be related to interparticle order. However, our understanding of the nonequilibrium pair correlation function is not as developed. Because system dynamics will now influence interparticle order, the analogy with atomic systems is no longer viable. When solvent hydrodynamic effects can be ignored, as in dilute but strongly interacting colloidal particle suspensions, there is a correspondence in behavior with computer simulations of atomic systems.[5] When hydrodynamic effects cannot be ignored, as in concentrated suspensions, atomic theory and computer simulations of atomic systems may not accurately predict nonequilibrium pair correlations or observed structure.

Several analytic theories for the nonequilibrium pair correlation function, or equivalently, the nonequilibrium static structure factor have been developed for colloidal suspensions subjected to shear flow. These theories involve various levels of approximation, which limit the range of applicability. The most rigorous theory is given by Batchelor (B)[6] for the pair distribution function as a perturbation expansion in shear rate about equilibrium using exact two-body expressions for the hydrodynamic interactions. The

theory is exact in the limit of small shear rates and small volume fraction of suspended particles. Batchelor's work has been extended to finite volume fractions by Russel and Gast (RG)[7] and Wagner and Russel (RW).[8] Within the formalism outlined by Felderhof,[9] these theories include exact pair hydrodynamics but evaluate the cluster expansion in thermodynamic interactions via approximate closures on the three-body equilibrium and nonequilibrium distribution functions. Russel and Gast incorporated the concentration dependent equilibrium structure, which arises naturally through the potential of mean force, but truncated the cluster expansion at the pair level, i.e., neglected explicit many-body couplings in the equation for the nonequilibrium structure. Wagner and Russel extended the treatment to account for these couplings through various closures for the three-body distribution function. Results from both superposition (RW-*S*) and Percus–Yevick (RW-PY) closure approximations will be examined. Subject to the validity of the closures, these theories predict the nonequilibrium deformation of an equilibrium microstructure calculated from the Percus–Yevick equation and determine suspension viscosities, elasticities and rheo-optical properties in the low shear limit.[8,10]

Another class of theories, which determines the static structure factor directly, has been developed by Ronis[11] and Hess.[12] These theories are far more approximate in the initial assumptions but produce estimates of the static structure factor for all shear rates and volume fractions. In the theory of Ronis, for example, a Langevin equation for the particle density is constructed from an effective diffusion equation. The time rate of change of the particle density is given by three terms: (1) Interparticle potentials and hydrodynamic interactions are contained in a diffusion term with a wave vector dependent diffusion constant. Identifying this diffusivity with that derived for equilibrium colloidal suspensions and measured by dynamic light scattering[2] provides a well defined theoretical form in terms of the equilibrium static structure factor and hydrodynamic interactions. (2) The shear flow is contained in a convective term. (3) The random force is assumed to be Gaussian correlated with wave

vector dependence given by the hydrodynamic factor in the diffusion constant. The theory was initially developed to describe light scattering results from dilute suspensions of colloidal particles undergoing shear flow.[13] In these systems hydrodynamic interactions are small and the theoretical predictions are in qualitative agreement with experiment. In more concentrated suspensions, where hydrodynamic interactions cannot be neglected, the theory (in its present form) is qualitatively different from the data at large rates of shear.[14]

Since all these theories are referenced to the equilibrium state, either as a perturbation about equilibrium or through an assumed form for a diffusion constant, we expect them to be most applicable in the small shear rate limit (e.g., near equilibrium) where the static structure factor, defined as a Fourier transform of the pair correlation function, has the form

$$S(\mathbf{k},\dot{\gamma}) = S(k,0)\{1 + \mathrm{Pe}\,\hat{k}_x\hat{k}_yA(k,\phi)\}. \tag{1.1}$$

Here the nonequilibrium static structure factor is given by $S(\mathbf{k},\dot{\gamma})$, the equilibrium static structure factor by $S(k,0)$, and the volume fraction by ϕ; the flow velocity direction is parallel to the unit vector $\hat{k}_x$ and the shear or velocity gradient direction to the unit vector $\hat{k}_y$. The Peclet number is defined by

$$\mathrm{Pe} = \dot{\gamma}a^2/D_0 = 6\pi\eta a^3\dot{\gamma}/k_BT. \tag{1.2}$$

Here η is the solvent viscosity, a is the particle radius (assuming uniform size), $\dot{\gamma}$ is the shear rate, and k_BT is the thermal energy. The function $A(k,\phi)$ depends on the theory under consideration and the scattered wave vector magnitude is given by

$$k = 4\pi n\sin(\theta/2)/\lambda. \tag{1.3}$$

Here n is the solvent index of refraction, θ is the scattering angle, and λ is the wavelength of the incident radiation. Note that the nonequilibrium static structure factor depends on the direction of $\mathbf{k}$, while the equilibrium static structure factor and $A(k,\phi)$ do not.

II. EXPERIMENTAL DATA

In this note we compare the predicted theoretical values for $A(k,\phi)$ with recent experimental measurements made on model "hard sphere" suspensions. These experiments have been reported in detail elsewhere,[14] but we briefly summarize the important experimental details here. The particles used in these experiments are $a = 79$ nm radius silica spheres (standard deviation to mean radius ratio $= 0.1$), sterically stabilized by a surface coating of octadecyl alcohol. The particles are suspended in cyclohexane which nearly matches the particle index of refraction and reduces multiple scattering to a negligible level. Furthermore, the particles in this solvent behave as hard spheres characterized by the Percus-Yevick theory[15] as indicated by other scattering experiments. The sample is confined between two parallel optically flat glass disks (gap spacing 0–0.052 cm). One disk (5 cm radius) rotates about its axis of symmetry to shear the sample. While the magnitude of the shear rate varies with distance from the axis of rotation, the sample is probed by light scattering only in a small region of width 0.03 cm at a distance of 4 cm from the axis of rotation. The incident light beam direction (633 nm wavelength) and scattered light detection direction are arranged so that the scattered wave vector $\mathbf{k}$ lies parallel to the local shear-velocity plane.

The scattered intensity is sampled at four distinct scattered wave vectors: $k_xa = \pm 0.46$, $k_ya = 0.49$, $k_za = 0.0$ [$ka = 0.67$] and $k_xa = \pm 0.97$, $k_ya = 0.64$, $k_za = 0.0$ [$ka = 1.16$], and we use the reduced wave vector units ka for hard sphere systems. The first two wave vectors are determined by fixing a scattering angle and then collecting intensity data for forward and reverse directions of disk rotation. The second set of wave vector data is collected at a different scattering angle in the same way. The magnitude of the scattered wave vector–particle radius product ka is much less than $\sim \pi$, the position of the first maximum in the theoretical static structure factor for hard spheres. In this sense the data correspond to small wave vector results, which probe particle ordering on a scale extending over several particle radii. However, the wave vector magnitude may not yet be small enough to measure a generalized "thermodynamic compressibility".

The scattered intensity is a product of the particle form factor and nonequilibrium structure factor. If the ratio of the nonequilibrium scattered intensity to the equilibrium scattered intensity is calculated, then the form factors cancel and this ratio may be compared directly with the predictions of the form given in Eq. (1.1) for low rates of shear. Here it is assumed that preferential ordering due to polydispersity effects is negligible. Figure 1 shows the intensity ratio for $\phi = 0.46$, $ka = 1.16$ and both directions of disk rotation ($k_x = \pm 0.97$) as a function of Pe. As predicted, the sign of the intensity change depends on rotation direction and initially changes linearly with shear rate. The slope of the linear portion determines $A(ka,\phi)$ for these parameters. In Figs. 2(a) and 2(b) are plotted the values of $A(ka,\phi)$ as a function of the particle volume fraction, for $ka = 0.67$ and $ka = 1.16$, respectively.
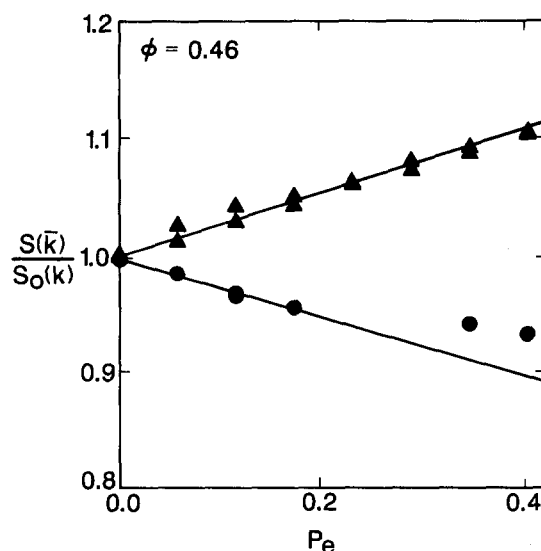

FIG. 1. Nonequilibrium to equilibrium static structure factor ratio as a function of Pe (shear rate) for a sample with volume fraction 0.46, $ka = 1.16$, $k_xa = 0.97$: ▲, and $k_xa = -0.97$: ●. The slope of the lines for each k_xa value gives estimates of A for these parameters.
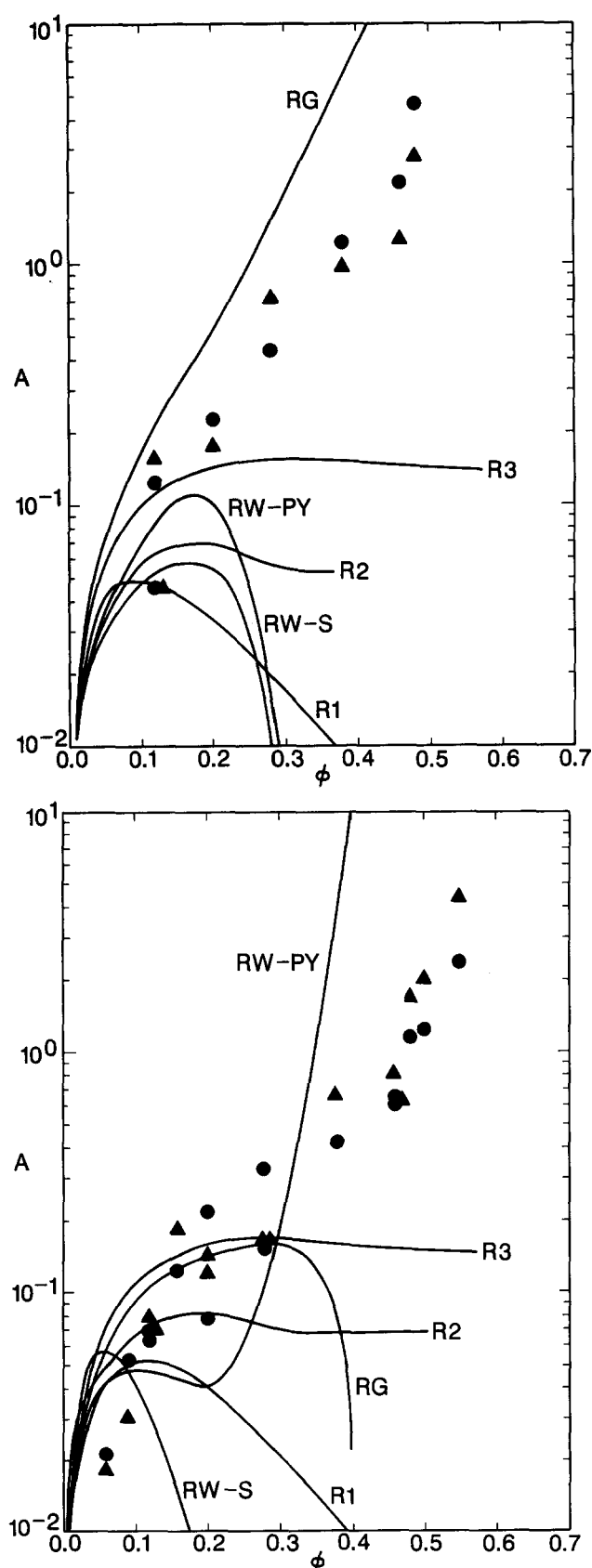
FIG. 2. Experimental values of A as a function of volume fraction for (a) $ka = 0.67$, $k_x a = 0.46$: ●, and $k_x a = -0.46$: ▲, and (b) $ka = 1.16$, $k_x a = 0.97$: ●, and $k_x a = -0.97$: ▲. Theoretical predictions are R1—Ronis theory; R2—Ronis theory times the ratio of the solution to the solvent viscosity; R3—Ronis theory times the equilibrium static structure factor; RG—Russel and Gast theory; RW-S—Russel and Wagner theory with the superposition closure; and RW-PY—Wagner and Russel theory with the Percus-Yevick closure.

The data for $A(ka,\phi)$ show a definite trend. As the volume fraction increases from 0 to 0.5, $A(ka,\phi)$ increases by orders of magnitude and is generally larger for the smaller value of ka. At a given magnitude of ka the data taken for the two directions of rotor motion generally agree, indicating the validity of the tensor or direction dependence of Eq. (1.1). The experimental error of the data comes primarily from estimates of the slope of the intensity data as presented in Fig. 1. There is error in any given intensity measurement and sufficient measurements must be taken at low shear rates to determine a reliable limiting value for the slope. This is particularly difficult at small volume fractions [$\phi < 0.1$] where the change in scattered intensity with shear rate is small and intensity fluctuations associated with rotor motion are of equal magnitude. Thus the experimental measurements have the largest error where the theoretical predictions are expected to be exact.

III. THEORETICAL PREDICTIONS

Figures 2(a) and 2(b) show several theoretical predictions of $A(ka,\phi)$ for hard spheres with radius a and no-slip boundary conditions. The equilibrium static structure factor used in evaluating the theories is taken to have the Percus–Yevick form. All theories reduce, in the small volume fraction limit, to the static structure factor calculated from Batchelor's exact solution for the nonequilibrium pair correlation function, though only the RG and RW theories actually reproduce these results exactly. The other theories do not contain the exact pair hydrodynamics. At larger volume fractions the RG and RW-PY theories give, perhaps, the best qualitative fit of the data for A. However, the theoretical values for A are very sensitive to the magnitude ka, having quite different behavior for the two values examined. At high volume fractions, A becomes negative in the RG theory for $ka = 1.16$, while the RW-PY theory predicts a negative A for $ka = 0.68$. The RW-S theory, based on the superposition closure for the many-body thermodynamics, predicts negative values for both sets of scattering vectors. On the other hand, the data never becomes negative, and it is observed that $A(ka = 0.67,\phi) > A(ka = 1.16,\phi)$.

The theory proposed by Ronis assumes a hydrodynamically dilute suspension with short time collective diffusion constant of [2,16]:

$$D_k = D_0/S(ka,0) , \qquad (3.1)$$

where D_0 is the infinite dilution diffusion constant. While these results as given in the figures appear qualitatively similar to the RW-S theory, the values for A always remain positive. To correct for hydrodynamic interactions in dense suspensions requires the following form for the short time collective diffusion constant [17]:

$$D_k = H(ka)/S(ka,0) . \qquad (3.2)$$

Experimental measurements [18] and theoretical calculations, [17] approximating higher order than pair correlation functions, find D_k for hard spheres to be weakly dependent on volume fraction, nearly equal to D_0 for all ϕ in the low ka limit. Evidently the increase in the thermodynamic driving force [$1/S(ka,0)$] nearly cancels an increase in hydrodynamic damping [$H(ka)$] as the volume fraction increases.

Thus we may correct (approximately) the predictions of Ronis theory by setting $D_k = D_0$, i.e., multiplying the results for A by $S(ka,0)$. These results fit to the data better, but still fail at large volume fractions. Values for A calculated by multiplying the Ronis results by the ratio of the suspension viscosity to the solvent viscosity at each volume fraction provide another estimate of the effect of hydrodynamics. These results are qualitatively similar to the previous calculations for obvious reasons, e.g., the hydrodynamic effects and the suspension viscosity increase with increasing volume fraction.

IV. CONCLUSIONS AND DISCUSSION

At low volume fractions ($\phi < 0.10$) the theoretical predictions all agree but depart from the limited experimental data, probably due to the difficulty in making accurate experimental measurements in this volume fraction region. As the volume fraction increases ($0.10 < \phi < 0.30$), the data become more reliable and there is rough agreement between theories and experiment. Some theories, RG, RW-PY, and Ronis times $S(ka,0)$, best estimate the experimental measurements. At the largest volume fractions ($\phi > 0.30$), only RG and RW-PY approximate the experimental measurements and then only for certain ka values.

The experiments probe correlations on a lengthscale of $ka \sim (2\pi a/r) \sim 1$, i.e., $r \sim 6a$ in the suspension. The statistical mechanical theories of Batchelor, Russel and Gast, and Russel and Wagner are averaged to the pair correlation level, with approximate closures for the higher order correlations, and, thus, might not accurately predict correlations over more than a few particle radii. Especially in dense suspensions, where three-body and higher correlations dominate, these theories which approximate many-body interactions in terms of effective pair correlations may err at $ka < 1$. This may explain some of the strong ka dependence of the predicted $A(ka,\phi)$ at moderate to high volume fractions. A more definitive test of these theories would be to probe near the major peak in the nonequilibrium structure factor.

It should be noted that conservative dichroism experiments probe the same region of the structure factor [i.e., $ka \sim 1.0$] as the light scattering results presented here, but yield contradictory results. While both experiments see linear behavior at similar Pe and dichroism experiments measure the orientation angle at 45°, the RW-S and RW-PY theories predict the dichroism reasonably at $\phi = 0.40$ but poorly at $\phi = 0.10$, in opposition to the light scattering results. It would be worthwhile to measure light scattering and dichroism on the same sample to resolve the conflict.

The low shear rate distortion of the static structure factor resembles that first observed in molecular dynamics computer simulations of atomic systems by Ashurst and Hoover.[19] In these simulations the distortion represents a competition between the applied shear moving the system away from equilibrium (related to the viscosity) and the relaxation of the system toward equilibrium [related to the compressibility represented by $S(ka,0)$]. At a given shear rate these two effects balance to produce a given distortion of the correlation function. The same intuition holds for the colloidal systems, except that the viscosity involves both particles and solvent. The failure of the colloidal theories to fit data at all volume fractions may be viewed as a failure of either the approximation for the viscosity effect, i.e., the hydrodynamic interactions, or the compressibility effect, i.e., the thermodynamic interactions. At large volume fractions the approximations in the hydrodynamic calculations may not be valid. Indeed self-diffusion calculations[17] show worse agreement with data[20] at large volume fractions. On the other hand, distortion of the fluid structure by the flow changes its compressibility properties. However, the observed structures appear to be small distortions of equilibrium structures, with significant structural changes only occurring at larger shear rates. The general approach outlined by Batchelor and Felderhof incorporates the intuition outlined above. The failure of these theories at higher volume fractions is a consequence of our current ignorance of many-body interactions in dense colloidal suspensions and not a flaw in the approach.

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