

Observations upon the dynamic structure factor of interacting spherical polyelectrolytes^{a)}

George D. J. Phillies

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109
(Received 17 January 1983; accepted 20 May 1983)

Experimental studies are reported on the light-scattering spectrum of 0.038 μ carboxylate-modified polystyrene latex spheres in deionized water. In concentrated suspensions, the long-time decay of the two-particle dynamic structure factor is given by a power law ($t^{-\alpha}$) form, not by a slow exponential. Nonlinear least squares fits found $\alpha \simeq 1.2$ – 1.5 , smaller values of α corresponding to higher sphere concentrations. The reduction of the mutual diffusion coefficient of 0.15 μ spheres in mixtures of 0.15 and 0.038 μ spheres was examined, and is interpreted in terms of the dynamic friction modification to the drag coefficients. Multiple scattering artifacts were shown to be absent with homodyne coincidence spectroscopy.

I. INTRODUCTION

Quasielastic light scattering has long been applied to the study of solutions of interacting monodisperse polyelectrolyte molecules.^{1,2} The concentration dependence of the slope $D_M k^2$ of the initial decay of the dynamic structure factor $S(k, t)$ was early given theoretical interpretation in terms of a concentration-dependent friction factor f and a thermodynamic factor related to the osmotic compressibility³ or the inverse of the static structure factor $S(k)$.^{4,5} Experimental confirmation of these equivalent theoretical interpretations was soon obtained.^{6–8} A careful examination of the form of $S(k, t)$ for nonideal macromolecule solutions revealed deviations at large t from single-exponential decay. The deviations were first expressed² in terms of the second cumulant of a cumulant expansion of $S(k, t)$; in other systems, these deviations have been described by a two-exponential model.^{9–11} A variety of interpretations of the long-time non-single-exponential behavior of $S(k, t)$ have been suggested, including memory function effects in the particle equations of motion,¹² a time-dependent contribution of particle-particle interactions to the drag coefficient,¹³ concentration-concentration mode-mode coupling terms in the diffusion equation, and polydispersity in either the interparticle interactions¹⁴ or the particle sizes.^{15,16}

We here report experimental studies on the light scattering spectra of suspensions of polystyrene latex spheres in deionized water. Our major objectives included a more careful study of the functional form of $S(k, t)$ at very long times, a study of multiple scattering effects with a homodyne coincidence spectrometer,¹⁷ and work on mixtures containing interacting polystyrene spheres of known, different sizes.

Experimental methods are treated in Sec. II. Experimental results are presented in Sec. III and interpreted in Sec. IV. Section V contains a discussion and summary.

II. METHODS

Studies were made of carboxylate-modified polystyrene latex spheres of nominal diameters 0.038 μ (Dow Pharm-

aceuticals) and 0.15 μ (Polysciences, Inc.). Light scattering spectra of dilute suspensions of these spheres in distilled nondeionized water found radii of 220 and 840 \AA , respectively. Deionized sphere suspensions were prepared in quartz fluorimeter cuvettes, four sides polished, by diluting known volumes of the sphere suspensions with 15 M Ω distilled water, adding specially cleaned mixed-bed ion-exchange resin, and aging for three to six weeks. It was at first found that samples deteriorated after several months, their spectra returning towards the forms observed before the ion-exchange resin was added. It was suspected that this effect was due to the slow leakage of CO₂ around the Teflon stoppers of the fluorimeter cuvettes. Coating the stopper rim, not at points in contact with the sample, with high-vacuum stopcock grease put an end to the progressive deterioration.

Spectra were taken of the 0.038 μ spheres at nominal sphere volume fractions of 1×10^{-4} , 5×10^{-4} , 1.3×10^{-3} , 2.5×10^{-3} , 3.8×10^{-3} , and 7.5×10^{-3} . Spectra were also obtained by mixtures of the 0.038 and 0.15 μ spheres, using the aforementioned concentrations for the 0.038 μ spheres, together with the 0.15 μ spheres at a nominal concentration of 6×10^{-5} by volume.

Our light scattering spectrometer incorporates a 25 mW HeNe laser, rigid optics based on a Newport Research vibration-isolation table, RCA 7265 photomultiplier tube coupled to Pacific Precision amplifier discriminator, and a 64 channel Langley-Ford Instruments digital correlator interfaced to a Data General Nova III computer. To obtain high resolution at short times and good signal-to-noise ratios at long times, it was necessary to make measurements on each sample using a series of different integration times and correlator channel spacings; overlapping spectra were then spliced. Several different splicing methods were tested, including (i) forcing all spectra to have a common base line (measured by delay channels in the correlator) and a common amplitude at a time t at which the signal-to-noise ratio of $S(k, t)$ was high, (ii) forcing agreement between spectral amplitudes at two well-separated delay times, using the base lines as free parameters, and (iii) graphical overlay and optical line fitting. All these methods give very similar results, though the optical method is modestly less precise than the alternate digi-

^{a)}The support of this work by the National Science Foundation under Grant CHE79-20389 is gratefully acknowledged.

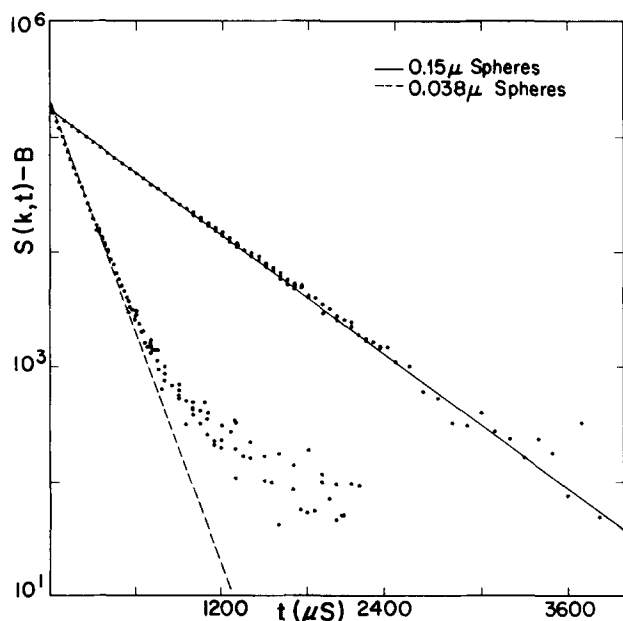


FIG. 1. Light scattering spectra of 0.038 (line, dots) and 0.15 μ (line, dots) carboxylate-modified polystyrene latex spheres in pure water, prior to removal of trace ions from the water. Sphere concentrations were $C_{0.038} = 0.02$ volume %, $C_{0.15} = 6 \times 10^{-3}$ volume %.

tal procedures. Error estimates were obtained by comparing results on single unspliced spectra with results on the merged spectra.

Spectra were fit to two functional forms. To obtain the limiting initial slope of $S(k, t)$ as $t \rightarrow 0$, and to study linear segments of more-complex spectra, we analyzed light scattering spectra, or their long or short time segments, by linear-least squares fit to a cumulant expansion

$$\frac{1}{2} \ln[S(k, t) - B] = \sum_{i=0}^n \frac{K_i (-t)^i}{i!}, \quad (1)$$

B being the base line and K_i being the i th cumulant. The long-time sections of spectra were also subject to the nonlinear least squares fit, using an optimized two-parameter mesh-scanning program, the assumed long-time form of the spectrum being

$$S(k, t) = a_0 t^{-b_0} + B. \quad (2)$$

The base line was determined experimentally. Multiple scattering effects were tested by means of the homodyne coincidence spectrometer described in Ref. 17.

III. RESULTS

By using multihour integration times, it was possible to obtain reasonably accurate measurements of the form of the spectrum $S(k, t)$ over several decades of its decay. Apparent signal-to-noise ratios near $t = 0$ of the order 1×10^3 were obtained. Control experiments in which the spectra of nondeionized sphere suspensions were measured with multihour integration times gave the expected spectra. Even with a multihour integration time, the spectrum of a constant signal (a piece of lens paper il-

luminated by a flashlight) was found to be essentially flat. The nonexponential spectra reported here for more concentrated systems are therefore interpreted as arising from physical effects in the sample, and not from laser noise or other artifacts.

Figure 1 shows spectra of the 0.038 and 0.15 μ carboxylate-modified polystyrene latex spheres, at low concentration, in distilled water to which ion-exchange resin had not been added. To within experimental error, the spectrum of the 0.15 μ spheres exhibits a single exponential curve over three orders of magnitude in the decay of $S(k, t)$. In particular, the exponential decay appears entirely linear in the time range (1–3 ms) and amplitude region [0.1%–10.0% of $S(k, 0)$] in which interesting effects are seen in the spectra of the concentrated deionized suspensions. The spectrum of the 0.038 μ spheres at low concentrations in untreated water does show a weak deviation from a single exponential. This deviation is not pronounced for $S(k, t) > 0.003 S(k, 0)$.

The effect of removing the background of small ions from the solvent is shown in Fig. 2. In this figure, one sees spectra of 0.038 μ polystyrene sphere suspensions of concentrations 0.05%, 0.25%, and 0.75% by volume. These suspensions were thoroughly deionized with specially cleaned ion exchange resin.

The spectrum of the 0.05% solution is consistent with a simple two-exponential model. Indeed, there are clear systematic differences between a power-law fit to this spectrum [Fig. 2(a), solid line] and the experimental data. In contrast, at high concentration, the spectrum is nonexponential at long times. In considering the 0.25% suspension, if one were to limit one's self to times $< 1500 \mu\text{s}$, the "long-time" part of $S(k, t)$ could be said to be a slow exponential, as indicated by the dashed line of spectrum 2(b). However, at times larger than $1800 \mu\text{s}$, the amplitude of the measured spectrum (dots) is visibly too large to be consistent with the slow-exponential characterization. One could use additional, even slower, exponentials to describe the spectrum at these very long times, but it would be very hard to determine such exponentials in a meaningful way. Alternatively one could impose a cutoff in time, and only fit $S(k, t)$ for times less than cutoff value, but exponentials obtained in this way would be artifacts of cutoff time.

In concentrated suspensions, mode-mode coupling effects may be significant, motivating consideration of the possibility that the long-time decay of $S(k, t)$ is described by a power law rather than an exponential. The hypothesis that $S(k, t)$ shows a long-term power law decay was tested by making a nonlinear least squares fit of $S(k, t)$, for $t > 900 \mu\text{s}$, to Eq. (2). Separate fits were made to each spectrum obtained on each sample. A simultaneous weighted fit of Eq. (2) to all the spectra on a given sample, using $S(k, 1 \text{ ms})$ of each spectrum as a weighing factor, was also made. The solid lines in Fig. 2 are the results of a simultaneous fit to all data. Unlike the dashed lines, the solid lines appear to be reasonable representations of $S(k, t)$ for concentrated suspensions at large time.

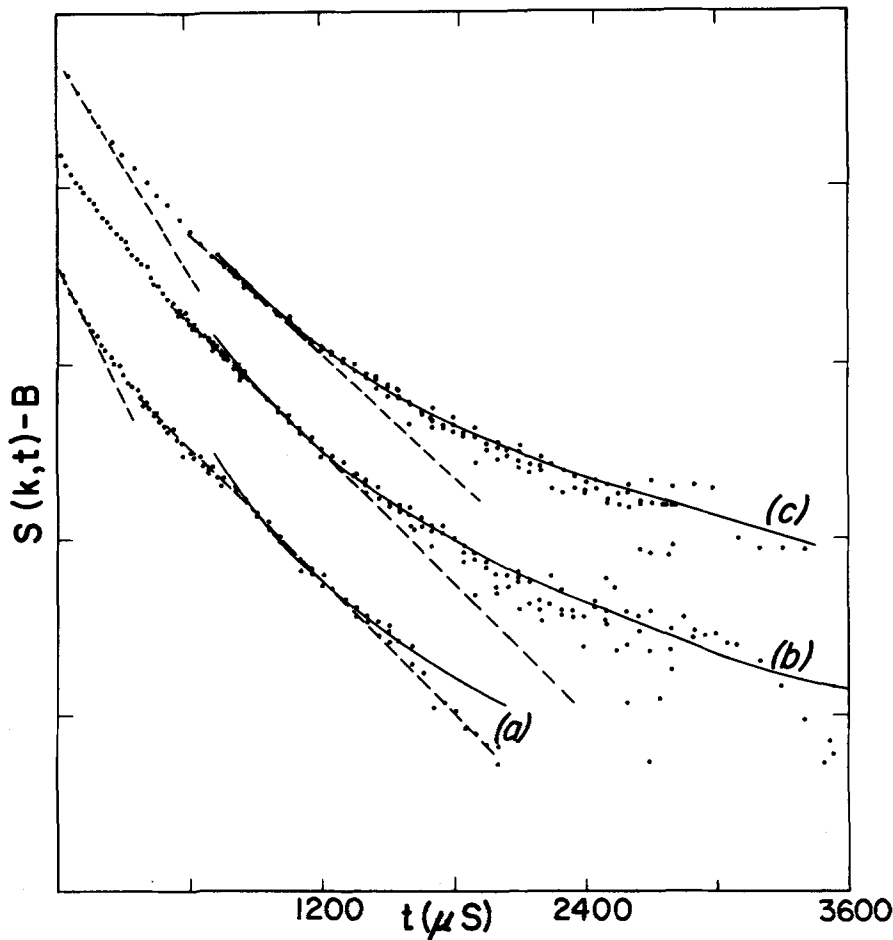


FIG. 2. Spliced light-scattering spectra $S(k, t)$ of 0.038μ polystyrene spheres at concentrations of (a) 0.02, (b) 0.25, and (c) 0.75 volume %, after removal of small ion contaminants with ion-exchange resin. The amplitude units are arbitrary. The dashed straight lines indicate the single-exponential decays which match limited regions of the spectra; solid curved lines indicate nonlinear least-mean-square fits of the spectra (for $t > 900 \mu s$) to a power law [Eq. (2)].

Figure 3 displays the decay coefficient b_0 of the long-time component of $S(k, t)$, as a function of the sphere concentration. b_0 decreases from 3.2 ± 0.1 at a sphere concentration of 0.13% to 2.45 ± 0.1 at a sphere concentration of 0.75%. At sphere concentrations below 0.1%, the form of $S(k, t)$ seems to be intermediate between a slow exponential and a power law. At these concentrations, one can still fit the long-time part of $S(k, t)$ to a power law decay, but deviations of the spectrum from the power-law form are systematic. b_0 for these concentrations was therefore not plotted in Fig. 3.

Several authors^{15,16} discuss the possibility that the long-time tail of $S(k, t)$ may be due to scattering polydispersity in the sample. Implicit in these models is the assumption that diffusional modes which exchange particles of differing scattering power ("tracer"-like models) are substantially hindered by direct and hydrodynamic interactions between the diffusing particles. To test this suggestion, mixtures containing a combination of 0.038μ spheres (at the concentrations used in the abovementioned experiments) and 0.15μ spheres (at a concentration of 6×10^{-5} by volume) were studied. As seen in Fig. 4, spectra of these samples show two clear exponentials. The faster, weak, exponential is not distinguishable in form from the decay spectrum of the 0.038μ spheres in the absence of 0.15μ spheres, though because of its low relative amplitude this weaker

decay can only be studied at relatively short times ($< 600 \mu s$). The dominant relaxational mode of the system is a slow single exponential whose decay time is similar to but less than that of the 0.15μ spheres in pure

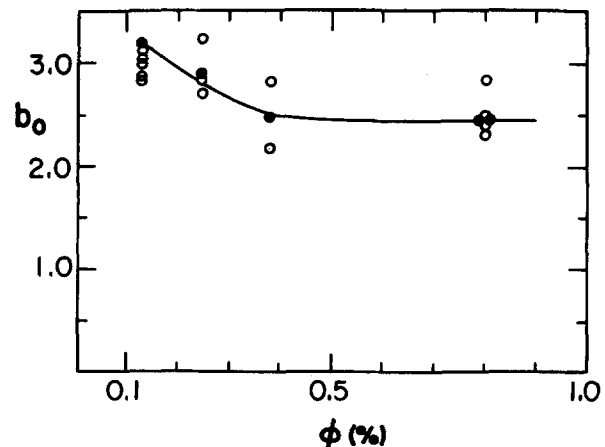


FIG. 3. Dependence of the power-law-decay coefficient b_0 , obtained by fitting spectra to Eq. (2), on the sphere concentration. Filled dots indicate fits to spliced spectra such as those shown in Fig. 2; open dots indicate fits of Eq. (2) for individual spectra. At very low concentrations, Eq. (2) is not a good representation of the long-time tail of $S(k, t)$ [Fig. 2(a) presents an example]; b_0 for these low concentrations has not been plotted.

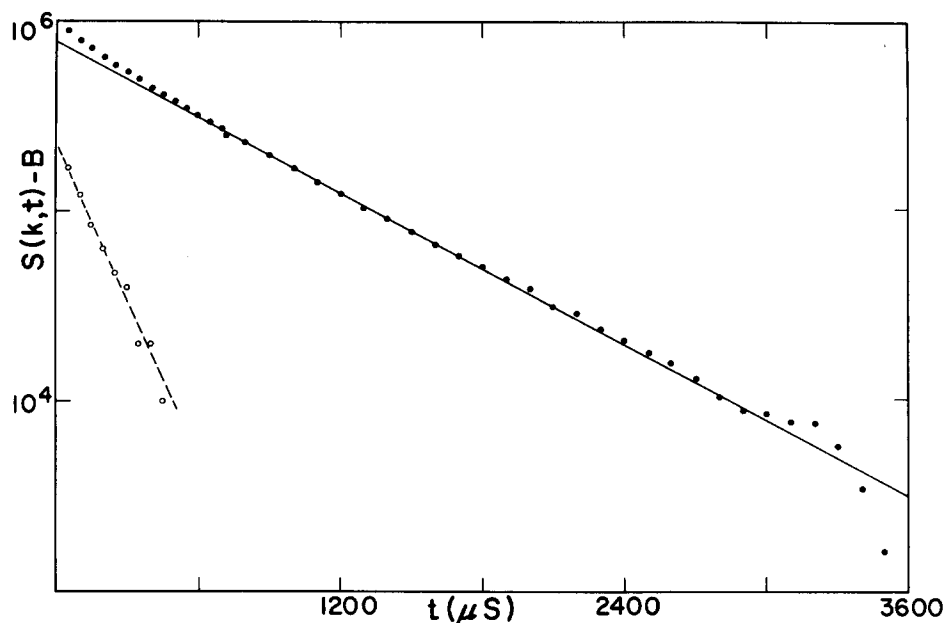


FIG. 4. Light scattering spectrum of a deionized mixture of 0.038 and 0.015 μ polystyrene spheres at concentrations of 0.38 and 0.006 volume %, respectively. The straight line is the long-time single exponential fit used to determine the diffusion coefficient D_T . The inset is the difference between the observed spectrum and a single slow exponential; this difference spectrum is not noticeably different in form from the spectrum of deionized 0.038 μ spheres at the same concentration.

water. We denote the diffusion coefficient deduced from this slow decay D_T .

Figure 5 shows D_T as a function of the concentration of the smaller (0.038 μ) spheres. Even at very high concentrations of the smaller spheres, direct measurement shows that the small spheres by themselves scatter much less light than the mixtures do, so the spectra are due primarily to scattering by the larger spheres. At very low small-sphere concentrations, D_T approaches the diffusion coefficient of the larger spheres in pure water. D_T falls with increasing small-sphere concentration. If one naively interprets D_T as arising from the motion of the larger spheres through the smaller, then, over the concentration range studied, the small spheres reduce the diffusion coefficient of the larger spheres by as much as 30%.

Polystyrene latex has an index of refraction increment which is substantially different from that of water. At higher sphere concentrations $S(k, t)$ might therefore be perturbed by multiple scattering. Since our objective is to study concentration effects, an extrapolation of data to zero concentration would not be helpful. Recourse was instead made to homodyne coincidence spectroscopy,¹⁷ a two-laser-beam, two-detector method for obtaining the single-scattering contribution to $S(k, t)$. As has previously been shown, homodyne coincidence instruments are immune to multiple scattering artifacts. Because our homodyne cross-correlation efficiency is of order 10%, our measurements of $S(k, t)$ at large t were appreciably less accurate with two detectors than with one detector. For small t , accurate measurements of the initial slope of $S(k, t)$ on deionized samples with homodyne coincidence are in good agreement with one-detector spectra, indicating that multiple scattering (which is expected to be most important at small t) is not significant. The absence of multiple scattering artifacts is consistent with the observation that the samples discussed in this paper are markedly

less turbid than the multiply scattering solutions studied in Ref. 17.

The scattering vector $|k|$ in this experiment was $1.87 \times 10^5 \text{ cm}^{-1}$, i. e., $|k|^{-1} = 535 \text{ \AA}$. For the 1×10^{-4} , 5×10^{-4} , 1.3×10^{-3} , 2.5×10^{-3} , 3.8×10^{-3} , and 7.5×10^{-3} volume fraction solutions, the mean interparticle distances may be estimated as 8800, 5100, 3700, 3000, 2600, and 2100 \AA , respectively, so that in this experiment particle motions were observed over distances short by comparison with the mean interparticle distance. A superficial examination of the scattered light intensity of angle revealed no sign of a maximum in the scattered intensity $S(k)$, but this phenomenon would not necessarily have been expected in our relatively dilute solutions.

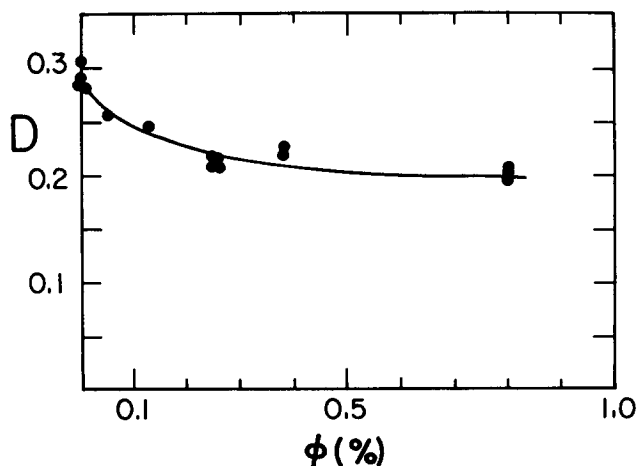


FIG. 5. Dependence of the diffusion coefficient D_T obtained from spectra of the 0.038/0.15 μ sphere mixtures on the concentration of the smaller spheres, the concentration of the larger spheres being held fixed. Also shown is the diffusion coefficient of the 0.15 μ spheres in a deionized solution in the absence of any 0.038 μ spheres. Diffusion coefficients are in units $10^{-7} \text{ cm}^2/\text{s}$.

IV. INTERPRETATION

Our first objective was to study the functional form of $S(k, t)$ at long times. As our spectra decrease monotonically and are convex upwards, they may presumably be represented, with good accuracy, as a sum of exponentials; Grüner and Lehman have used this approach. This paper treats an alternate representation for $S(k, t)$. Just as the two-exponential approximation for $S(k, t)$ suggests several^{11,18} theoretical models for these solutions, alternate representations of $S(k, t)$ —such as the power-law form successfully tested here—may suggest other pictures of a macroparticle suspension.

Our scattering volume was much larger than the static and dynamic correlation ranges of the system, so the central limit theorem indicates that the scattering intensity is a Gaussian random process. $S(k, t)$ is then related to the density $\rho_k(t)$ of scatterers by

$$S(k, t) - B = \left\langle \left| \sum_{i,j=1}^N b_i b_j \exp\{ik \cdot [r_i(0) - r_j(t)]\} \right|^2 \right\rangle \\ \equiv \langle \rho_k(0) \rho_{-k}(t) \rangle^2, \quad (3)$$

B being the base line, b_j and $r_j(t)$ being the scattering cross section and the position at time t of the scatterer j , and ρ_k being the k th spatial Fourier component of the scatterer density.

$S(k, t)$ was found to be concentration dependent, passing from one exponential at extreme dilution to a two-exponential form at low sphere concentrations and a power-law decay at higher concentrations. From Eq. (3), the concentration-concentration correlation function $\langle \rho_k(0) \rho_{-k}(t) \rangle$ must also be described by a two-exponential form at low concentration and by a power-law ($t^{-1.2}$ to $t^{-1.6}$) decay at high concentration and large t . The similarity between our high concentration data and the theoretical long-time $t^{-3/2}$ decays, characteristic of mode-coupling effects, suggests but does not prove that concentration-concentration mode coupling effects are important.

Theories for $S(k, t)$ for strongly interacting suspensions are largely not helpful in understanding our results. Most work has emphasized the first time cumulant of $S(k, t)$ in systems sufficiently dilute that only interactions between isolated pairs of particles are significant. At least two calculations^{19,20} of the second time cumulant of $S(k, t)$ have been made, albeit for a model system without hydrodynamic interactions. While either of these inequivalent calculations can be iterated to obtain higher-order time cumulants, interpreting our data would require an unreasonably great number of iterations. Furthermore, the observed power-law decay is not experimentally correct at short times (indeed, it is not analytic at $t=0$), so an expansion of $S(k, t)$ as a Taylor series around $t=0$ can only give numerical agreement with our findings. In addition to these difficulties, mode-coupling terms involve the effects of interacting trios of particles, i. e., they are only important at second and higher orders in the concentration. The published calculations^{21,22} of the $O(C^2)$ corrections to D are only for the initial slope or the low-frequency limit of D .

Several authors^{18,23} have used the Zwanzig-Mori formalism to calculate $S(k, t)$. The difficult part of

these computations is finding a form for the Mori memory kernel $M(k, t)$. For example, if $M(k, t)$ is an exponential, $S(k, t)$ is a double exponential. Forms for $M(k, t)$ resulting in $S(k, t) \sim t^{-\alpha}$ at large t seem not to have been treated.

The data represented by Figs. 1–3 does not conclusively determine whether the long-time tail of $S(k, t)$ is due to interactive effects or to polydispersity. Current theories of interacting suspensions do not treat $S(k, t)$ at long times; while there are plausibility arguments, a quantitative comparison of experiment and prediction is presently impossible. Published work^{15,24} on polydispersity predicts a long time slow exponential, not a $t^{-\alpha}$ form, but this is clearly an artifact of the approximations used in that work. If a solution contained trace quantities of particles having a range of sizes, the solutions's spectrum would exhibit a range of slow exponentials, whose sum could readily mimic a power-law decay. Our results therefore do not disprove the conjecture that the $t^{-\alpha}$ tail is caused by polydispersity.

Our second objective was to study scattering from bidisperse suspensions. Weissman's proposal¹⁵ on polydispersity effects gave one motivation for this work. Arguments¹³ that dynamic friction (which results from the correlation between the Brownian movements of a particle and the subsequent interparticle forces on that particle) hinders both mutual and self-diffusion gave another motivation.

The scattering spectrum of a solution containing two interacting macroparticle species was computed a decade ago.²⁵ Pusey²⁴ and this author²⁶ have treated the special case in which the two species are identical except for their scattering cross sections. The bidisperse suspensions reported here form an alternate special case, in which the scattering is dominated by a species whose concentration is vanishingly small. As shown in Appendix A, if one ignores mode-coupling terms the scattering spectrum for this special case is

$$[S(k, t) - B]^{1/2} = \exp(-D_A k^2 t) \left\{ I_A - \frac{D_{BA}}{D_B - D_A} I_{AB} \right\} \\ + \exp(-D_B k^2 t) \left\{ I_B + \frac{D_{BA}}{D_B - D_A} I_{AB} \right\}. \quad (4)$$

Here A is the dilute, intensely scattering species, D_A is the self-diffusion coefficient of A through the A - B mixture, D_B is the mutual diffusion coefficient of B in the absence of A , and I_A and I_B are the scattering intensities due to species A and B , respectively, including interference effects due to correlations between molecules of the two species. The I_{AB} terms results from a dynamic effect in which the cross-diffusion coefficient D_{BA} (which gives the current in B due to a concentration gradient of A) transfers intensity from one relaxational mode to the other; I_{AB} vanishes if either species scatters no light.

Equation (4) justifies our interpretation of Figs. 4 and 5 by predicting that the dominant slow exponential describes the self-diffusive motion of the highly dilute 0.15 μ spheres ("A" component) through a concentrated background of more weakly scattering 0.038 μ spheres ("B" component). Equation (4) predicts that the weak, rapid-

ly decaying exponential of the mixtures should match the spectrum of the 0.038 μ spheres in the absence of 0.15 μ spheres. This was found experimentally. Equation (4) is based on a linear two-component theory so it can not predict long-time tails, regardless of one's model for them. Since the long-time decays of Fig. 2 would be too weak to see in Fig. 4, and deionized 0.15 μ spheres at $\phi \approx 6 \times 10^{-5}$ have a single-exponential spectrum, the absence of long-time nonexponential effects in Fig. 4 is unsurprising.

As seen in Fig. 5, the 0.038 μ spheres act to reduce the self-diffusion coefficient D_T of 0.15 μ spheres in mixtures. Mazur and vanSaarloos²⁷ have recently obtained the 2, 3, and 4-point hydrodynamic interaction tensors for spheres of different sizes, so the expected hydrodynamic effect of the smaller spheres on the motions of the larger ones is readily obtained (cf. Appendix B) as the approximation:

$$D_T = D_{15}^0 \left(1 - \frac{15}{4} \phi_{38} \left[\frac{a_{15}}{\sigma_{15} + \sigma_{38}} \right] \right), \quad (5)$$

D_{15}^0 being the diffusion coefficient of an isolated 0.15 μ sphere, ϕ_{38} being the volume fraction of the 0.038 μ spheres (in our mixtures, $\phi_{38} < 0.01$), a_{15} being the hydrodynamic radius of the 0.15 μ particles, and σ_{15} and σ_{38} being the radii of exclusion of the 0.15 and 0.038 μ particles. To obtain Eq. (5), the charged hard spheres were approximated as neutral hard spheres with an enhanced distance of closest approach $\sigma_{15} + \sigma_{38}$, $\sigma_{15} + \sigma_{38}$ being larger than the hydrodynamic diameter $a_{15} + a_{38}$. The effect of charging is to reduce the hydrodynamic correction in Eq. (5); if the spheres were neutralized, the effect of hydrodynamics on D_T would be increased. Equation (5) predicts a dependence of D_T on ϕ_{38} which is much less than the apparent initial slope visible in Fig. 5, so the dependence of D_T on ϕ_{38} is largely not due to hydrodynamic interactions between the larger and smaller spheres.

One explanation of the concentration dependence of D_T is that the motion of the larger spheres is hindered by dynamic friction, due to the fluctuating forces exerted on the larger spheres by the smaller ones. It has been shown theoretically¹³ that such fluctuating forces between diffusing macroparticles enhance the friction factors f for mutual and tracer diffusion, so this effect has the right sign to account for the failure of Eq. (5). Indeed, Hess and Klein,²⁸ beginning with a Focker-Planck equation, recently used projection operators and a mode-mode coupling formalism to obtain the modification of the self-diffusion coefficient of a charged sphere by direct interactions. The calculation, which neglects hydrodynamic interactions, uses the static structure factor measured by Grüner and Lehmann.¹¹ Hess and Klein obtain for the concentration dependence of D_s a plot qualitatively identical to Fig. 5.

V. DISCUSSION

It is perhaps surprising that we find a $t^{-\alpha}$ form for $S(k, t)$ at large t , rather than the slow exponential reported by others. If Weissman's polydispersity interpretation is correct, the variations in $S(k, t)$ may sim-

ply reflect differences in the macroparticle size distribution function and thus may not be physically important. Furthermore, unless one goes to extremely large times, a power law decay looks much like an exponential; with some spectra, power-law and exponential fits will both be qualitatively acceptable. Contrariwise, to show that one does have a single slow exponential, and not a power-law decay, one must obtain high-quality data for times appreciably greater than those needed to calculate the apparent decay constant of the exponential.

The diffusion of very dilute 0.15 μ spheres is retarded by 0.038 μ spheres, the extent of the retardation being much greater than that expected from the hydrodynamic interactions between the spheres. Hess and Klein,²⁸ using an equation substantially identical to our form¹³ for the dynamic friction effect on the diffusion coefficients, calculated the concentration dependence of a quantity similar to D_T . While some details are different, the qualitative agreement between their theoretical numbers and our data is excellent.

The diffusion of interacting macroparticles of differing sizes and scattering cross sections has been extensively studied by Kops-Werkhoven *et al.*,²⁹ who obtain results in many respects similar to those reported here. In their system, which was a suspension of neutral hard spheres, increasing the concentration (up to 50 volume %) resulted in two-exponential spectra and in changes in the mutual and tracer diffusion coefficients of the spheres. The differences in $S(k, t)$ in between Ref. 29 and the results here could be due to the long range of the forces between charged spheres.

ACKNOWLEDGMENT

I wish to thank Dr. Alan Hurd for his gift of pretreated ion exchange resin.

APPENDIX A: LIGHT-SCATTERING SPECTRA OF TWO-INTERACTING MACROCOMPONENT MIXTURES

Reference (25) obtains the quasielastic light scattering spectrum of a three-component (solvent, solute A, solute B) system whose diffusion obeys the linear flow equations

$$\frac{d}{dt} a_A(k, t) = -\Gamma_A a_A(k, t) - \Gamma_{AB} a_B(k, t),$$

$$\frac{d}{dt} a_B(k, t) = -\Gamma_{BA} a_A(k, t) - \Gamma_B a_B(k, t),$$

where

(A1)

$$\Gamma_A = D_A k^2, \quad \Gamma_B = D_B k^2, \quad \Gamma_{AB} = D_{AB} k^2, \quad \Gamma_{BA} = D_{BA} k^2,$$

k is the scattering vector, and $a_i(k, t)$ is the amplitude of the k th spatial Fourier component of the concentration of i . The spectrum of this solution is predicted to be

$$\begin{aligned} \langle I(0)I(t) \rangle - B = I_0 A^{-1} (\Gamma^+ - \Gamma^-)^{-1} & (e^{-\Gamma^+ t} \{ (\Gamma_A - \Gamma^-) (\epsilon_a^2 \alpha + \epsilon_a \epsilon_b \gamma) \\ & + (\Gamma^+ - \Gamma_A) (\epsilon_b^2 \beta + \epsilon_a \epsilon_b \gamma) + \Gamma_{AB} (\epsilon_a^2 \epsilon_b \alpha + \epsilon_b^2 \gamma) \} \\ & + e^{-\Gamma^- t} \{ (\Gamma^+ - \Gamma_A) (\epsilon_a^2 \alpha + \epsilon_a \epsilon_b \gamma) + (\Gamma_A - \Gamma^-) (\epsilon_a \epsilon_b \gamma + \epsilon_b^2 \beta) \\ & - \Gamma_{AB} (\epsilon_a^2 \gamma + \epsilon_a \epsilon_b \beta) - \Gamma_{BA} (\epsilon_a \epsilon_b \alpha + \epsilon_b^2 \gamma) \}), \end{aligned} \quad (A2)$$

where heterodyne detection is assumed,

$$\Gamma^{\pm} = \frac{1}{2}(\Gamma_A + \Gamma_B) \pm \left\{ \left[\frac{1}{2}(\Gamma_A - \Gamma_B) \right]^2 + \Gamma_{AB}\Gamma_{BA} \right\}^{1/2},$$

$$a_0 = a_A(k, 0),$$

$$b_0 = a_B(k, 0).$$

$$A = \epsilon_A^2 \alpha + 2\epsilon_A \epsilon_B \gamma + \epsilon_B^2 \beta, \quad (\text{A3})$$

$$\alpha = \langle |a_A(k, 0)|^2 \rangle,$$

$$\beta = \langle |a_B(k, 0)|^2 \rangle,$$

$$\gamma = \langle |a_A(-k, 0)a_B(k, 0)| \rangle.$$

ϵ_A and ϵ_B being the optical scattering lengths (the cross sections being ϵ_A^2 , ϵ_B^2) for the two species.

In our system, the strong interactions arise from the great range of the forces. The hydrodynamic volume of either species is small, so reference frame corrections³⁰ are negligible. This approximation would be poor for $\phi \geq 10\%$. From Ref. 25, Sec. 4, Ref. 3, Sec. 4 and an integration by parts, the diffusion coefficients are

$$D_{ij} = \frac{K_B T [\delta_{ij} + c_i h_{ij}(k)]}{f_i}, \quad (\text{A4})$$

where δ_{ij} is a Kronecker delta, f_i is the drag coefficient of species i in the solution of interest, c_i is the concentration of i , and $h_{ij}(k)$ is the spatial Fourier transform of the i - j radial distribution function.

In our special case, $D_B > D_A$, $\epsilon_A > \epsilon_B$, $N_A \epsilon_A^2 \gg N_B \epsilon_B^2$ (but the scattering by B does not vanish, so $N_B \epsilon_B^2 > 0$), and $C_A \approx 0$. On neglect of terms in C_A , Eq. (A2) reduces to Eq. (4), where

$$I_A = \epsilon_A^2 N_A + \epsilon_A \epsilon_B N_A C_B h_{AB}(k),$$

$$I_B = \epsilon_B^2 N_B [1 + C_B h_{BB}(k)] + \epsilon_A \epsilon_B N_B C_A h_{AB}(k),$$

$$I_{AB} = \epsilon_A \epsilon_B N_A + \epsilon_B^2 N_A C_B h_{AB}(k),$$

$$D_A = \frac{k_B T}{f_A}, \quad (\text{A5})$$

$$D_B = \frac{K_B T [1 + C_B h_{BB}(k)]}{f_B},$$

$$D_{BA} = \frac{C_B h_{AB} K_B T}{f_B}.$$

Reference 25 shows that D_A is the tracer (self) diffusion coefficient of A in the mixture while D_B is the mutual diffusion coefficient of species B.

APPENDIX B: DIFFUSION COEFFICIENT OF ONE COMPONENT OF A MIXTURE

Our objective is to obtain the diffusion coefficient D_A of a highly dilute species A in the presence of a concentrated background of a second species B; both species are charged spherical particles. For simplicity, the effect of Debye-screened electrostatic interactions will be approximated by treating the particles as neutral hard spheres whose hydrodynamic radii a_H are consistently less than their exclusion radii a_V . That is, the electrical forces keep the spheres touching each other. The initial slope of the dynamic structure factor of the A particles, neglecting interactions between pairs of A particles, gives D_A as

$$-D_A k^2 S_{AA}(k, 0) = \lim_{t \rightarrow 0} \frac{d}{dt} \left\langle \frac{1}{N_A} \sum_{i, j=1}^{N_A} \exp[i\mathbf{k} \cdot [\mathbf{r}_j(0) - \mathbf{r}_i(t)]] \right\rangle, \quad (\text{B1})$$

$\mathbf{r}_i(t)$ being the location of the i th of the N_A A particles.

Equation (B1) is evaluated to first order in concentration by following Ref. 22. Dividing particle velocities into their Brownian and interactive parts, $\mathbf{v}_i = \mathbf{v}_{B_i} + \mathbf{v}_{I_i}$, in the small-time limit $t \rightarrow 0$, Eq. (B1) becomes

$$-D_A k^2 S_{AA}(k, 0) = \frac{1}{N_A} \left\langle \sum_{i, j=1}^{N_A} \exp[i\mathbf{k} \cdot \mathbf{r}_{ji}(0)] \left\{ -i\mathbf{k} \cdot \mathbf{v}_i(t) - \int_0^{t \rightarrow 0} ds [\mathbf{k} \cdot \mathbf{v}_{B_i}(s) \mathbf{k} \cdot \mathbf{v}_{B_i}(t) + \mathbf{k} \cdot \mathbf{v}_{B_i}(s) \mathbf{k} \cdot \mathbf{v}_{I_i}(t)] \right\} \right\rangle. \quad (\text{B2})$$

Comparison with Ref. 22, Eqs. (4.1)–(4.4), and use²⁷ of Mazur's hydrodynamic interaction tensors for a pair of spheres of radii a_i and a_j , separated by r_{ij} ,

$$\mu_{ii} = \frac{1}{6\pi\eta a_i} \left[1 - \frac{15}{4} \frac{a_i^3}{r_{ii}^3} \hat{\mathbf{r}}_{ii} \hat{\mathbf{r}}_{ii} \right], \quad (\text{B3a})$$

$$\mu_{ii} = \frac{1}{6\pi\eta a_i} \left[\frac{3}{4} \frac{a_i}{r_{ii}} (\mathbf{1} + \hat{\mathbf{r}}_{ii} \hat{\mathbf{r}}_{ii}) + \frac{a_i^3 + a_i a_i^2}{4r_{ii}^3} (\mathbf{1} - 3\hat{\mathbf{r}}_{ii} \hat{\mathbf{r}}_{ii}) \right], \quad (\text{B3b})$$

lets one write

$$i\mathbf{k} \cdot \mathbf{v}_{I_i} = \frac{i\mathbf{k}}{f_i} \left[1 - \frac{15}{4} \sum_{i=1}^{N_A+N_B} \frac{a_i a_i^3 \hat{\mathbf{r}}_{ii} \hat{\mathbf{r}}_{ii}}{r_{ii}^3} \right] \cdot \mathbf{F}_i + \frac{i\mathbf{k}}{f} \quad (\text{B4a})$$

$$\cdot \sum_{i=1}^{N_A+N_B} \left[\frac{3}{4} \frac{a_i}{r_{ii}} (\mathbf{1} + \hat{\mathbf{r}}_{ii} \hat{\mathbf{r}}_{ii}) + \frac{a_i^3 + a_i a_i^2}{4r_{ii}^3} (\mathbf{1} - 3\hat{\mathbf{r}}_{ii} \hat{\mathbf{r}}_{ii}) \right] \cdot \mathbf{F}_i,$$

$$\int_0^{t \rightarrow 0} \mathbf{k} \cdot \mathbf{v}_{B_i}(s) \mathbf{k} \cdot \mathbf{v}_{B_i}(t) ds = \frac{k_B T}{f_i} \left[1 - \frac{15}{4} \sum_{i=1}^{N_A+N_B} \frac{a_i a_i^3}{r_{ii}^3} \right] k^2, \quad (\text{B4b})$$

where $f_i = 6\pi\eta a_i$ and F_i is the direct force on particle i . The $\int \mathbf{v}_{B_i}(s) \mathbf{v}_{I_i}(t) ds$ term, which causes dynamic friction, is discussed in Sec. IV of this paper.

Equations (B2)–(B4) are combined and regrouped to separate terms which only depend on the presence of the A particles from terms which arise from the B particles. Since species A is highly dilute, all A–A interactions are set to zero [so $S_{AA}(k, 0) = 1$]. The A–B radial distribution function is approximated as

$$g_{AB}(r) = 0, \quad r < \sigma_A + \sigma_B, \quad (\text{B5})$$

$$g_{AB}(r) = 1, \quad r \geq \sigma_A + \sigma_B,$$

where $\sigma_A > a_B$ and $\sigma_B > a_B$. To first order in C_B , the only effect of the B particles on D_A is through Eq. (B4b). Equation (B4a) vanishes because each term either involves the negligible A–A forces or cancels by spherical symmetry. The remaining integral shows

$$D_A = D_A^0 \left(1 - \frac{15}{4} \phi_B \left[\frac{a_A}{\sigma_A + \sigma_B} \right] \right) - \int \hat{\mathbf{k}} \cdot \mathbf{v}_{B_i}(s) \hat{\mathbf{k}} \cdot \mathbf{v}_{I_i}(t) ds. \quad (\text{B6})$$

Here ϕ_B is the hydrodynamic volume fraction of B particles, D_A^0 is the diffusion coefficient of the A particles

in the absence of the B particles and k is a unit vector. Equation (B6), less the dynamic friction integral, is Eq. (5).

- ¹P. N. Pusey, D. W. Schaeffer, D. E. Koppel, R. D. Camerini-Otero, and R. M. Franklin, *J. Phys. (Paris)* **33**, C1-163 (1972).
- ²P. Doherty and G. B. Benedek, *J. Chem. Phys.* **61**, 5426 (1974).
- ³G. D. J. Phillies, *J. Chem. Phys.* **60**, 974 (1974).
- ⁴P. N. Pusey, *J. Phys. A* **8**, 1433 (1975).
- ⁵B. J. Berne, in *Photon Correlation Spectroscopy and Velocimetry*, edited by H. Z. Cummins and E. R. Pike (Plenum, New York, 1977).
- ⁶S. S. Alpert and G. Banks, *Biophys. Chem.* **4**, 287 (1976).
- ⁷G. D. J. Phillies, N. M. Mazer, and G. B. Benedek, *J. Chem. Phys.* **65**, 1883 (1976).
- ⁸R. S. Hall, Y. S. Oh, and C. S. Johnson, Jr., *J. Phys. Chem.* **84**, 756 (1980).
- ⁹P. N. Pusey, *J. Phys. A* **11**, 119 (1973).
- ¹⁰P. S. Dalberg, A. Boe, K. A. Strand, and T. Sikkeland, *J. Chem. Phys.* **69**, 5473 (1978).
- ¹¹F. Gruner and W. Lehmann, in *Light Scattering in Liquids and Macromolecular Solutions*, edited by V. DeGiorgio, M. Corti, and M. Giglio (Plenum, New York, 1982).
- ¹²W. Hess and R. Klein, *Physica* **94A**, 71 (1978).
- ¹³G. D. J. Phillies, *J. Chem. Phys.* **74**, 2436 (1981); *Chem. Phys.* **74**, 197 (1983).
- ¹⁴G. D. J. Phillies, *Macromolecules* **9**, 447 (1976).
- ¹⁵M. B. Weissman, *J. Chem. Phys.* **72**, 231 (1980).
- ¹⁶P. N. Pusey, in Ref. 11.
- ¹⁷G. D. J. Phillies, *J. Chem. Phys.* **74**, 260 (1981); *Phys. Rev. A* **24**, 1939 (1981).
- ¹⁸W. Hess and R. Klein, *J. Phys. A* **13**, L5 (1980).
- ¹⁹B. J. Ackerson, *J. Chem. Phys.* **64**, 242 (1976).
- ²⁰G. D. J. Phillies and P. R. Wills, *J. Chem. Phys.* **75**, 508 (1981).
- ²¹C. W. J. Beenakker and P. Mazur, *Phys. Lett.* **91**, 290 (1982).
- ²²G. D. J. Phillies, *J. Chem. Phys.* **77**, 2623 (1982).
- ²³W. Hess, in Ref. 11.
- ²⁴P. N. Pusey, H. M. Fijnaut, and A. Vrij, *J. Chem. Phys.* **77**, 4270 (1982).
- ²⁵G. D. J. Phillies, *J. Chem. Phys.* **60**, 983 (1974).
- ²⁶G. D. J. Phillies, *Biopolymers* **14**, 499 (1975).
- ²⁷P. Mazur and W. van Saarloos, *Physica A* (in press).
- ²⁸W. Hess and R. Klein, *J. Phys. A* **15**, L669 (1982).
- ²⁹(a) M. M. Kops-Werkhoven and H. M. Fijnaut, *J. Chem. Phys.* **74**, 1618 (1981); (b) M. M. Kops-Werkhoven, H. J. Mos, P. N. Pusey, and H. M. Fijnaut, *Chem. Phys. Lett.* **81**, 365 (1981); (c) M. M. Kops-Werkhoven and H. M. Fijnaut, *J. Chem. Phys.* **77**, 2242 (1982); (d) M. M. Kops-Werkhoven, C. Pathmanoharan, A. Vrij, and H. M. Fijnaut, *ibid.* **77**, 5913 (1982); (e) M. M. Kops-Werkhoven, A. Vrij, and H. N. W. Lekkerkerker, *ibid.* **78**, 2760 (1983).
- ³⁰J. G. Kirkwood, R. L. Baldwin, P. J. Dunlap, L. J. Gosting, and G. Kegeles, *J. Chem. Phys.* **33**, 1505 (1960).