Diffusion and Structure in Dense Binary Suspensions

P. D. Kaplan and A. G. Yodh
Physics Department, University of Pennsylvania, Philadelphia, Pennsylvania 19104

D. J. Pine
Exxon Research and Engineering Company, Annandale, New Jersey 08801
(Received 21 August 1991)

Model colloids composed of two widely separated sizes of polystyrene spheres are studied at high volume fractions using an optical, multiple-scattering technique. These measurements probe hydrodynamic forces between unlike particles, as well as static, structural predictions made using the Percus-Yevick approximation. The dynamic data corroborate currently available hydrodynamic theories on very short length scales; the dynamic data also reveal a new, experimentally accessible range of intermediate length scales which currently available theories cannot explain.

PACS numbers: 82.70.Dd, 05.40.+j, 42.20.−y, 61.20.Gy

Asymmetric binary colloids present fundamental geometric questions about particle packing and interparticle forces. In contrast to uniform dispersions, binary colloids contain two distinct types of particles whose interaction depends on their relative size [1]. This extra degree of freedom introduces a complex, short-range order that can produce a much richer variety of phases at the solidification point [2] and in the pure liquid [3]. Particle-size asymmetry also leads to instabilities and new dynamic structures in sedimenting colloids [4]. The character of these dynamic structures is controlled by the hydrodynamic interactions between different particles. In equilibrium systems, these same hydrodynamic interactions determine the Brownian diffusivity of particles and, therefore, set the time scale of the kinetics for phase transitions.

While hydrodynamic interactions between particles in polydisperse systems have attracted considerable theoretical attention in recent years, there has been little experimental work [2,5–7] that critically tests emerging theories [8]. Surprisingly, few experimental studies have tested the static structure of highly asymmetric, binary, hard-sphere systems [5], although predictions based on the Percus-Yevick approximation have been available for some time [9]. This situation has arisen, in part, because traditional optical techniques are difficult to apply to dense colloids as a result of strong multiple light scattering. In this paper we present new diffusing-wave spectroscopy (DWS) [10] experiments which exploit multiple light scattering to probe diffusion and structure in dense, binary hard-sphere suspensions. This information is extracted within DWS theory by modeling photon transport as a random walk. Our work explicitly probes the hydrodynamic coupling between *unlike* spheres and thus represents a first step towards elucidating the role of particle-size asymmetry and concentration in multicomponent diffusion theories. In addition, we probe the structure of highly asymmetric, binary mixtures of hard spheres at high densities and test calculations of the static partial structure factors determined within the Percus-Yevick approximation for widely separated particle sizes. Finally, we extend the theory of DWS to strongly interacting binary colloids.

A first glance at the data highlights the importance of interparticle dynamics and interparticle ordering. Measurements were made on three mixtures of polystyrene spheres with the same ratio of diameters but different average particle size (Table I). Measured differences between the systems are a result of the dependence of DWS on the ratio of particle size to wavelength. In each system, the volume fraction of large spheres ϕ_L is held constant and the volume fraction of small spheres ϕ_S is varied. In Fig. 1 we plot the reciprocal of the photon random-walk step length $1/l^*$ as a function of ϕ_S. This quantity, $1/l^*$, is analogous to the resistivity of a binary liquid alloy [11]. In the first approximation these graphs are straight lines; that is, the optical resistivity is proportional to the number density of scatterers. Deviations from straight lines are a result of particle ordering, which decreases the optical resistivity. The effects of ordering are most remarkable in the smallest system where $1/l^*$ actually *decreases* with the addition of scattering particles. In Fig. 2 the effective diffusion coefficient D_{eff} normalized to the value for a system with no small spheres is plotted as a function of small-sphere volume fraction ϕ_S. Notice that D_{eff} first increases with ϕ_S and then begins to decrease. This unusual behavior is the result of two mechanisms: the increasing contribution of small parti-

TABLE I. To probe similar physics on different length scales, we study three systems with the same ratio of particle diameters but different absolute sizes.

	Small	Medium	Large
a_L (μm)	0.205	0.625	2.00
a_S (μm)	0.065	0.205	0.625
$\alpha \equiv a_S/a_L$	0.32	0.33	0.31
ϕ_L	0.045	0.051	0.102
$k_0 a_L$	3.3	10.1	32.2

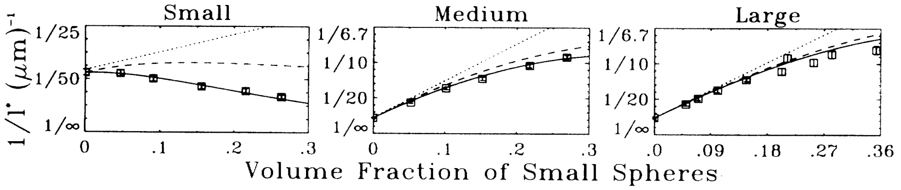

FIG. 1. Measurements of the reciprocal photon transport mean free path $1/l^*$ show the effects of interparticle structure. Calculations using the full PY binary hard-sphere structure factors (solid line) agree with the data and differ most from a noninteracting theory (dotted line) and a theory without interspecies structure [14] (dashed line) when the particles are smaller than the wavelength of the probe.

cles to the scattering as ϕ_S is increased and the hydrodynamic coupling between large and small particles. Our measurements represent the first experimental determination of this coupling.

To measure l^* and $D_{\rm eff}$, we employ standard DWS techniques. Samples in 0.5- or 1.0-mm-thick cuvettes are illuminated from one side by the 514-nm line of an Ar-ion laser, and the intensity of a single speckle of transmitted light is monitored. By comparing the average intensity to known monodisperse samples, we deduce l^* [12].

Using l^*, we extract an effective diffusion coefficient from the first cumulant of the measured intensity autocorrelation functions, whose time dependence is proportional to the square of the field autocorrelation function $g_1(\tau)\equiv\langle E(\tau)E^*(0)\rangle/\langle|E|^2\rangle$. For multiply scattered light, DWS theory gives [10]

$$g_1(\tau)=\int_0^\infty P(s)\exp\left[-2\frac{s}{l^*}k_0^2D_{\rm eff}\tau\right]ds\,, \tag{1}$$

where $P(s)$ is the fraction of detected photons that traveled a distance s through the sample and k_0 is the laser wave vector in the solvent. The spheres are polystyrene suspended in water. We estimate the screening length of the polystyrene spheres in suspension to be ~40 Å so that the interparticle potential is essentially hard sphere.

Two aspects of binary colloids are important for understanding our measurements: *static* particle ordering and *dynamic* particle diffusion in the presence of other particles. The static problem is solved using only the hard-sphere interaction potential to calculate l^*. A full solution of the dynamic problem requires knowledge of particle hydrodynamics *and* interparticle structure.

The static problem can be reduced to the calculation of interparticle partial structure factors in a binary system [13]. Within the diffusion approximation for photon transport, the key quantity is the photon random-walk step length l^*, which depends on the number of scattering events needed to randomize the direction of a photon; this number depends on the scattering properties of individual particles as well as spatial correlations between particles [14,15]. A general expression for l^* is [14,16]

$$l^*=k_0^6a^4\left[\pi\rho\int_0^{2k_0a}I(q)q^3dq\right]^{-1}, \tag{2}$$

where ρ is the number density of particles, a is the particle diameter, and $\mathbf{q}=(\mathbf{k}_0-\mathbf{k}_f)a$ is the dimensionless momentum transfer for a single-scattering event. In a monodisperse system, $I(q)$ is simply the product of the form and structure factors $F(q)S(q)$. In a binary system, we still calculate l^* using Eq. (2), but now we replace ρ with $\rho_L+\rho_S$, a with a_L (following the convention of Ref. [17]), and $I(q)$ with

$$I(q)\rho=S_{LL}(q)F_L(q)\rho_L+S_{SS}(q)F_S(q)\rho_S+2S_{LS}(q)\mathrm{Re}(f_L(q)f_S^*(q))(\rho_L\rho_S)^{1/2}, \tag{3}$$

where $F(q)=|f(q)|^2$ and $f(q)$ is the dimensionless, far field, single-scattering amplitude. The partial structure factors are defined as a sum over all particle positions $\mathbf{r}_i^\alpha$ and $\mathbf{r}_j^\beta$ of types α and β:

$$S_{\alpha\beta}(q\neq0)=\left\langle\sum_{ij}\exp[i\mathbf{q}\cdot(\mathbf{r}_i^\alpha-\mathbf{r}_j^\beta)/a_L]\right\rangle\Big/(N_\alpha N_\beta)^{1/2}.$$

Since $F(q)$ is known from Mie scattering theory, the only missing elements of the calculations of l^* are the partial

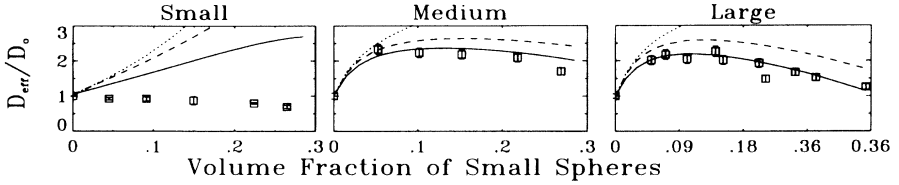

FIG. 2. Hydrodynamic interactions decrease the effective diffusion constant. The solid line is the fully coupled theory, with $m_{\alpha\beta}$ given by Eq. (6). The dashed line ignores forces between balls of different sizes ($m_{\alpha\beta}=\delta_{\alpha\beta}B/2$), and the dotted line ignores forces between particles ($m_{\alpha\beta}=0$). The dramatic failure of the theory for the small system indicates the importance of having a full wavelength-dependent hydrodynamic theory.

structure factors, which measurements of l^* directly probe.

Of the many schemes available for calculating the thermodynamic properties of disordered systems, the Percus-Yevick (PY) approximation has an analytic solution for dense hard-sphere systems. Our calculations of l^*, based on the PY structure factors [17], are presented with the data in Fig. 1. For the small and medium particle-size systems, the theory is in excellent agreement with the data; for the large particle-size system, the agreement is still quite satisfactory although PY overestimates $1/l^*$ by approximately 10% for $\phi_S \gtrsim 0.2$. To illustrate the importance of using the full structure factor, we also plot the results of a calculation which ignore all interparticle structure $[S_{\alpha\beta}(q)=\delta_{\alpha\beta}]$ and results which ignore just correlations between particle species $[S_{LS}(q)=0]$.

The difference between data sets results solely from the different cutoffs in the integral over $I(q)q^3$ in Eq. (2). By varying particle size, we probe the q dependence of $I(q)$. Measurements in the small system reveal the most about the long-range structure of the colloid because they are sensitive to relatively low q. Conversely, measurements in the large system reveal the most about the local structure of the colloid. With the exception of computer simulations [7], our work is one of the few experimental tests of PY for a dense, highly asymmetric, hard-sphere system. The excellent agreement for l^* indicates that the $I(q)$ used in Eq. (3) is reasonable.

We consider the dynamic problem by building a multiple-scattering theory from a single-scattering result. In a single-scattering photon correlation experiment, D_{eff} is extracted from the first cumulant of $g_1(\tau)$. Following the derivation of Ref. [18] for monodisperse colloids and *ignoring hydrodynamics*, we find for binary mixtures [15]

$$D_{\text{eff}}(q)=\frac{D_{L0}F_L(q)\rho_L+D_{S0}F_S(q)\rho_S}{I(q)\rho}, \tag{4}$$

where D_{L0} and D_{S0} are single-particle Einstein diffusion coefficients. This result is valid on time scales which are long compared to the particles' viscous damping times and short compared to the time it takes a particle to diffuse an interparticle spacing. Note the absence of an interspecies diffusion coefficient D_{LS} in Eq. (4). This term appears only after including hydrodynamic effects, and even then, it is diminished by a multiplicative factor $S_{LS}(q)$, which approaches 0 at large q. In a multiple-scattering experiment all wave vectors contribute, and the observed diffusion coefficient is obtained by averaging Eq. (4) over all scattering angles:

$$D_{\text{eff}}=\frac{D_{L0}[F_L(q)]\rho_L+D_{S0}[F_S(q)]\rho_S}{[I(q)]\rho}, \tag{5}$$

where $[X(q)]=\int_0^{2k_0a_L}Xq^3\,dq$ [19]. The dot-dashed line in Fig. 2 shows that calculations of D_{eff} based on Eq. (5) inadequately describe our data at all but the smallest ϕ_S. To improve our description of the data, we must include the hydrodynamic interactions between particles.

Since the hydrodynamic force between two particles depends on their separation [20], the particle diffusion coefficients in Eq. (4) are q dependent. Unfortunately, there are at present no calculations for the q dependence of $D_L(q)$ and $D_S(q)$ [21]. However, the infinite-q limit, where $D(q)$ is equivalent to the short-time self-diffusion coefficient, has been calculated by Batchelor [1]. To linear order in the volume fraction, the self-diffusion coefficients in a binary system are given by

$$\begin{bmatrix} D_L/D_{L0} \\ D_S/D_{S0} \end{bmatrix} = \mathbb{1} - \begin{bmatrix} m_{LL} & m_{LS} \\ m_{SL} & m_{SS} \end{bmatrix} \begin{bmatrix} \phi_L \\ \phi_S \end{bmatrix}, \tag{6}$$

where Batchelor's calculations indicate that the hydrodynamic coupling constants are $m_{\alpha\beta} \simeq B/(1+a_\beta/a_\alpha)$ with $B \approx 3.75$ [22]. This beautifully simple result had never been experimentally tested. Since we lack a q-dependent theory for binary systems, we incorporate hydrodynamic interactions by inserting the infinite-q result of Eq. (6) into Eq. (5). Note that the q^3 in the averages of Eq. (5) weight our measurements towards large q where $D(q)$ approaches $D(\infty)$ [19]; thus, our approximation should be asymptotically correct when the upper cutoff of the integrals in Eqs. (2) and (5) is large. We vary this upper cutoff $2k_0a_L$ by changing the absolute particle sizes by a factor of 10 while keeping the relative particle sizes in each mixture constant. Thus, changing the particle size effectively probes the q dependence of the dynamics, that is, of $D_{\text{eff}}(q)$.

The measurements of D_{eff} in Fig. 2 show the effect of increasing the concentration of small particles. For the two larger systems, D_{eff} rises as the diffusion of the smaller, faster particles becomes dominant. At higher volume fractions, the hydrodynamic couplings cause D_{eff} to decrease. Part of this decrease results from hydrodynamic interactions between similar particles. To see this, compare the dotted lines, calculated without hydrodynamic coupling ($m_{\alpha\beta}=0$), to the dashed lines, calculated without interspecies coupling ($m_{\alpha\beta}=\delta_{\alpha\beta}B/2$). The theory with the full hydrodynamic coupling (solid lines) demonstrates that interspecies hydrodynamic coupling is significant for nearly all nonzero ϕ_S. By varying the coupling coefficient B in the off-diagonal elements of Eq. (6) and leaving the well-tested diagonal elements [16,19,23] at their exact value of 1.83 [1], we find that the data are best fitted by $B=5.6\pm1.4$ in the medium system and $B=3.7\pm0.4$ in the large system. Batchelor's predicted value is $B=3.75$. Batchelor's expression is valid for the infinite-q, large-k_0a_L limit; thus it is not surprising that it fails to describe the small-particle system, where $k_0a_L=3.3$. By contrast, Batchelor's theory describes the data well for the large-particle system, where $k_0a_L=32$.

We conclude that Batchelor's expressions appear to possess the correct concentration and asymmetry dependence in the limit for which they are intended (infinite q)

and that a q-dependent theory for the hydrodynamic interaction is essential to understand smaller systems. Our results illustrate that multiple-scattering spectroscopies are practical probes of polydisperse systems and may be of further use in understanding the dynamics and kinetics of glass formation, freezing, and phase separation in complex fluids.

We gratefully acknowledge discussions with F. C. MacKintosh, T. C. Lubensky, and J. Z. Xue. This work was supported by the National Science Foundation through Grant No. DMR-9003687. A.G.Y. acknowledges partial support from the NSF through the PYI program and from the Alfred P. Sloan Foundation.

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