Final Project Report for NAG3-1852

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The four-year grant NAG3-1852 pertaining to "Studies of particle sedimentation by novel scattering techniques" began May 1, 1996 (5-1-96 to 4-30-00, $100,000/year). We have finished 4 major research projects and published 10 papers during this grant period. An important aspect of this research has been the education of students at graduate and undergraduate levels. They have been fully involved in the research described below.

1. Polymer-induced depletion interaction in colloid-polymer mixtures

Microscopic interactions between colloidal particles in polymer solutions control the phase stability of many colloid-polymer mixtures, which are of direct interest to industries. Lubricating oils and paint are examples of the colloid-polymer mixtures, in which phase stability is desired. The study of the colloid-polymer mixtures is also of fundamental interest in statistical physics. The recent theoretical calculations[1–4] for the entropy-driven phase separation in binary mixtures of hard spheres have stimulated considerable experimental efforts to study the phase behavior of various binary mixtures, such as liquid emulsions,[5] binary colloidal mixtures,[6–9] colloid-surfactant mixtures,[10] binary emulsions,[11] and mixtures of colloid with non-adsorbing polymer.[12] Measurements of phase behavior and other thermodynamic properties are useful in studies of macroscopic properties of the binary mixtures, but they are much less sensitive to the details of the molecular interactions in the system. Microscopic measurements, such as radiation-scattering experiments, therefore become important to verify assumptions and test predictions of various theoretical models for the depletion effect.[13,14] The study of microscopic interactions complements the macroscopic measurements. With the knowledge of the microscopic interactions, one can estimate the phase stability properties of the binary mixtures in a straightforward way. (The reverse process of inferring the inter-molecular interactions from the phase behavior is much more problematic and unsure.)

In contrast to many previous experimental studies,[15,16] which mainly focus on the phase behavior of the colloid-polymer mixtures, we have recently carried out a comprehensive small-angle neutron scattering study of the depletion interaction between colloidal particles, when they are suspended in adsorbing and non-adsorbing polymer solutions. By matching the scattering length density of the solvent with that of the polymer, we measured the colloidal (partial) structure factor, which is directly related to the colloid interaction potential. For the first time, the scattering data in the non-adsorbing polymer solution show a quantitative agreement with the theoretical prediction for the depletion interaction. The magnitude of the attraction is found to increase linearly with the polymer concentration but it levels off at higher polymer concentrations. This reduction in the depletion attraction can be explained by the screening of the interaction between the polymer chains at high concentrations. The scattering results from the adsorbing end-functionalized polymer solution reveal that the end-functionalized polymer chains partition themselves between the bulk solution and the adsorbed state. The free polymer molecules in the solution introduce a depletion attraction between the colloidal particles, but the magnitude of the attraction is reduced considerably by the adsorbed polymer chains on the colloidal surfaces. The experiment demonstrates the effectiveness of using adsorbing and non-adsorbing polymers to control the colloidal interaction and to study interaction-related phenomena in different colloidal systems. With the ability of tailoring the microscopic interaction between the colloidal particles, one can control the macroscopic phase properties of many colloid-polymer mixtures, which are of direct interest to industries.

This work has been presented in several invited talks in technical conferences and research institutes and has resulted in following publications:

(1) "Neutron Scattering Study of Depletion Interactions in a Colloid-Polymer Mixture," X. Ye, T. Narayanan, P. Tong, and J. S. Huang, Phys. Rev. Lett. **76**, 4640 (1996).

(2) "Depletion Interactions in Colloid-Polymer Mixtures," X. Ye, T. Narayanan, P. Tong, J. S. Huang, M. Y. Lin, B. L. Carvalho, and L. J. Fetters, Phys. Rev. E. **54**, 6500 (1996).

(3) "Interactions in Mixtures of a Microemulsion and a Polymer," K.-Q. Xia, Y.-B. Zhang, P. Tong, and C. Wu, Phys. Rev. E. **55**, 5792 (1997).

(4) "Neutron Scattering Study of Colloidal Interactions in an Adsorbing Polymer Solution," X. Ye, P. Tong, and L. J. Fetters, Macromolecules, **30**, 4103 (1997).

2. Colloidal sedimentation in polymer solutions

In recent years there has been a growing interest in studying microrheological properties of complex fluids containing macromolecules of different architectures. Examples include gels,[17,18] foams,[19] emulsions,[20] and various biomaterials, such as DNA, polymeric actin and cell extracts.[21,22] The study of local viscoelastic properties of these biomaterials at scales comparable to the molecular dimensions is of fundamental interest in statistical physics and is also relevant to many biological processes, such as cell morphogenesis, division, and macromolecular transport.[23,24] Various experimental techniques have been developed recently for the study of the microrheological properties and many of them involve the measurement of the motion of probe particles suspended in the medium of interest.[17,25–28] Our work focuses on the transport of probe particles in semidilute polymer solutions. The colloid-polymer system is simpler, because the particles behave like hard spheres and the polymer chains form a fluctuating network, whose spatial structure is well understood.[29] Although many investigations have been carried out to study the motion of small particles in various polymer solutions,[30–38] the experimental situation is complicated by the polymer adsorption, electrostatic interactions, and other effects that are peculiar to the system under study.[33]

With the well-characterized colloid-polymer system discussed in Sec. 1, we varied the microscopic interaction between the particle and the polymer molecule and studied its effect on particle sedimentation and diffusion. In the experiment, we measured the particle sedimentation velocity $v_c(\phi_c, C_p)$ as a function of the colloid volume fraction ϕ_c and the polymer concentration C_p. The experiment reveals that in the dilute colloidal suspension, the particles "feel" the single-chain viscosity rather than the solvent viscosity when their hydrodynamic radius R_h becomes smaller than the correlation length ξ of the polymer solution. The particles experience the macroscopic viscosity of the polymer solution when $R_h >> \xi$. The measurements clearly demonstrate the existence of a sharp transition near the crossover polymer concentration and its universal feature provides a benchmark, against which future theoretical models can be tested. In the concentrated colloid-polymer mixture, the measured $v_c(\phi_c, C_p)$ shows a large effect of the depletion interaction on colloidal sedimentation. The sedimentation data from the concentrated samples are found to be well described by the Batchelor's theory,[39] once the depletion interaction is taken into account. By varying the microscopic interaction between the colloidal particle and the polymer molecule, we find three different behaviors toward the Stokes-Einstein equation in the same colloid-polymer system.

Because the basic molecular interactions are chosen to be simple, we are able to explain the three different behaviors consistently in terms of the microstructures formed in the colloid-polymer mixture. The experiment, therefore, provides a coherent picture, which resolves some of the long-standing disputes in the field.

This work has been presented in several invited talks in technical conferences and research institutes and has resulted in following publications:

(1) "Sedimentation of Colloidal Particles through a Polymer Solution," P. Tong, X. Ye, B. J. Ackerson, Phys. Rev. Lett. **79**, 2363 (1997).

(2) "Colloidal Sedimentation in Polymer Solutions," X. Ye, P. Tong and L. J. Fetters, Macromolecules, **31**, 6534 (1998).

(3) "Transport of Probe Particles in Semidilute Polymer Solutions," X. Ye, P. Tong and L. J. Fetters, Macromolecules, **31**, 5785 (1998).

3. Velocity fluctuations in particle sedimentation

In the sedimentation experiment discussed in Sec. 2, we used small colloidal particles. Their spatial positions are determined by Brownian motion and thermodynamic interactions, such as the depletion attraction between the particles. For large particles, however, the effect of thermal agitations is negligible and their spatial distribution is determined by the hydrodynamic interactions, as well.[40] Sedimentation of non-Brownian particles under gravity through a quiescent fluid represents an anomalous diffusion process, in which hydrodynamic dispersion coefficients might diverge.[40,41] The main issue in sedimentation is to understand how hydrodynamic interactions created by the motion of many surrounding particles affect a test particle's mean sedimentation velocity $\bar{v}$ and its variance $\widetilde{\delta v}$ at different particle concentrations.[15] Because the hydrodynamic interaction decays as $1/r$ for large interparticle separations r, simple theoretical calculations[42] as well as computer simulations[43] have indicated that $\widetilde{\delta v}$ might diverge with increasing sample size L. Experiments, however, find no dependence of $\widetilde{\delta v}$ on L.[44,45] Solving the divergence problem, therefore, has become a profound issue in the study of particle sedimentation.[40,41,46]

Recently, we proposed a new theoretical model to describe concentration and velocity fluctuations in particle sedimentation. The model assumes that the small-scale motion of the particles is controlled by hydrodynamic diffusion and their large-scale motion is determined by convection. Regions having more particles become heavier than the average and they can induce velocity fluctuations in the suspension. With a new set of coarse-grained equations of motion, we find that particle sedimentation is analogous to turbulent convection at high Prandtl numbers. Using a mixing-length theory,[47] we obtain scaling relations for the characteristic length and velocity in sedimentation. These scaling laws as a function of particle radius a and volume fraction ϕ are in excellent agreement with the recent experiment by Segrè et al.[48] Our model gives a simple interpretation for the existence of a velocity cut-off length and thus resolves the long-standing divergence problem in sedimentation. The theory also provides a coherent framework for the separation of length scales involved in the sedimentation dynamics.

This work has stimulated considerable interests in the field and recently we have been chosen to give an invited presentation on this subject at the Centennial Meeting of American Physical Society (March 20-26, Atlanta, 1999). The work was published recently in Physical Review E, Rapid Communication:

"Analogies between Colloidal Sedimentation and Turbulent Convection at High Prandtl Numbers," P. Tong and B. J. Ackerson, Phys. Rev. E, **58**, R6931, 1998.

We are now preparing a long paper on concentration and velocity fluctuations at different length scales in particle sedimentation.

4. New laser light scattering techniques for velocity difference measurements

In the theoretical calculation discussed in Sec. 3, we find that the particle motion in sedimentation is analogous to the fluid motion in turbulent thermal convection. In studies of turbulence, one is often interested in measuring the velocity *difference*, $\delta\mathbf{v}(\mathbf{r}) = \mathbf{v}(\mathbf{x}) - \mathbf{v}(\mathbf{x}+\mathbf{r})$, over varying length $\mathbf{r}$, rather than the local velocity $\mathbf{v}(\mathbf{x})$. As was demonstrated many years ago,[49–51] $\delta\mathbf{v}(\mathbf{r})$ is accessible by homodyne photon correlation spectroscopy (PCS). Unlike laser Doppler and other velocimetry methods, PCS can measure the velocity difference directly without invoking Taylor's "frozen turbulence" assumption[52,53] to interpret the measurements. Over the past decade, we have used the PCS technique to explore small-scale turbulence in various flow geometries and resulted in a series of publications.[54–58] With the PCS technique, small seed particles that follow the local flow of the fluid scatter light from a laser. A photodetector records the scattered light intensity $I(t)$, which fluctuates due to the motion of the seed particles. The output signal of the detector is, therefore, modulated at a frequency equal to the difference in Doppler shifts of all particle pairs in the scattering volume. For each particle pair separated by a distance r (along the beam propagation direction), this Doppler shift difference is $\mathbf{q} \cdot \delta\mathbf{v}(r)$ where $\mathbf{q}$ is the momentum transfer vector. With the homodyne method, one measures the intensity auto-correlation function[59]

$$g(\tau) = \frac{\langle I(t+\tau)I(t)\rangle}{\langle I(t)\rangle^2} = 1 + bG(\tau), \tag{1}$$

where b (≤ 1) is an instrumental constant.

It has been shown that the function $G(\tau)$ has the form[54]

$$G(\tau) = \int_0^{\ell} dr\ h(r) \int_{-\infty}^{\infty} d\delta v\ P(\delta v, r) \cos(q\tau\delta v), \tag{2}$$

where $P(\delta v, r)$ is the probability density function of the velocity component δv in the direction of $\mathbf{q}$, and $h(r)dr$ is the number fraction of particle pairs separated by a distance r in the scattering volume. The scattering volume viewed by the photodetector is assumed to be quasi-one dimensional with its length ℓ being much larger than the beam radius σ. In the previous experiments, ℓ was varied by changing the width S of a slit in the collecting optics. Because of the limitations on the collecting optics, the range of ℓ which could be varied in the experiment was only approximately 1 decade (typically from 0.15 to 1.0 mm). The lower cut-off for ℓ is controlled by σ, and the upper cut-off is determined by the "coherence area" on the detecting surface of the photodetector, over which the scattered electric fields are strongly correlated in space.[59] When S becomes too large, the photodetector sees many temporally fluctuating "speckles" (or coherence areas), and consequently fluctuations of the scattered intensity will be averaged out over a range of q values ($= q_0 \pm \Delta q$) spanned by the detecting area. For spatially uncorrelated particle motions, such as Brownian diffusion, this spatial averaging over Δq only affects the signal-to-noise ratio of the measured $G(\tau)$, but the decay rate of $G(\tau)$ remains unchanged.[59] In turbulent and other self-similar flows, however, particle motions at different points are strongly correlated and the spatial averaging effect changes both the signal-to-noise ratio and the functional form of $G(\tau)$.[51,60]

To improve the PCS technique, we studied the effect of changing the slit width S and the magnification factor M of the scattering volume on the correlation function $G(\tau)$. The measured $G(\tau)$ is found to be of scaling form for different values of M provided S is kept below a critical value S_c. Accordingly a convenient collecting optics was devised to expand the variable range of ℓ up to 2 decades, over which $\delta\mathbf{v}(\ell)$ can be measured accurately. This new scheme increases the variable range of ℓ, but the weighted average over r in Eq. (2) is still required because the photodetector receives light from particle pairs having a range of separations $(0 < r \leq \ell)$.[61] To eliminate the average over r and obtain information about $P(\delta v, r)$ directly from the measured $G(\tau)$, we developed a new fiber-optic method, which uses a "double-slit" arrangement instead of the usual "single-slit" arrangement for PCS. In the experiment, two single mode, polarization preserving fibers are used to collect light with the same scattered wavevector $\mathbf{q}$ but from two spatially separated regions in a sample. These regions are illuminated by a single coherent laser beam, so that the collected signals interfere when combined using a fiber optic coupler, before being directed to a photodetector. With the unique design of the fiber-optic method, we remove the upper limit for ℓ based on the scattering geometry and extend it to the coherence length of the laser. The new technique revolutionizes the optical design of PCS for the measurement of $\delta v(\ell)$, so that one can directly obtain information about $P(\delta v, \ell)$ over a wide range of ℓ. The method will be very useful for the study of turbulent and other self-similar flows, such as that in particle sedimentation, in which one is interested in testing the scaling laws of $\delta\mathbf{v}(\ell)$ over varying ℓ.

We have presented this work in several conferences and research institutes, and the project has resulted in following publications:

(1) "Measurement of the Velocity Difference Using Photon Correlation Spectroscopy - an Improved Scheme,"T. Narayanan, C. Cheung, P. Tong, W. I. Goldburg, and X.-L. Wu, Applied Optics, **36**, 7639 (1997).

(2) "Velocity Difference Measurement Using a Fiber-Optic Coupler,"Yixue Du, B. J. Ackerson, and P. Tong, J. Opt. Soc. Am. A. **15**, 2433 (1998).

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