CONF-850871--6

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CONF-850871--6

DE85 016294

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STRUCTURE AND HYDRODYNAMICS OF COLLOIDAL SYSTEMS

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Solid State Division
OAK RIDGE NATIONAL LABORATORY
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MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
Oak Ridge, Tennessee 37831

July 1985

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Structure and Hydrodynamics o.
Colloidal Systems

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RUNNING TITLE:

Structure and Hydrodynamics of Colloids

KEYWORDS:

Small Angle Neutron Scattering
Neutron Spin-Echo
Colloids
Ferrofluids
Structure factor
Hydrodynamics

Abstract.

Colloidal phases (for example, micellar solutions, latex suspensions, ferrofluids and microemulsions) provide excellent model systems with which to test structural and hydrodynamic theories of the liquid state. Interparticle potentials may be attractive or repulsive, and the experimentalist is often free to control the strength, range and symmetry of the interactions. Small-angle neutron scattering (SANS) and small-angle neutron spin-echo (SANSE) provide excellent complementary tools for studying the structure and time-dependence of these systems, where correlation lengths typically vary from about one to several tens of nm. Correlation times are usually in the nsec to μ sec range, but may be of order minutes in certain systems. This paper will review some of the current theories and their recent experimental tests, using colloidal systems in which the direct interaction potentials may have spherical, dipolar or cylindrical symmetry and the hydrodynamic interactions may be weak or strong.

1. Introduction.

Colloidal suspensions typically exhibit spatial correlations over distances of order $1 - 10^3$ nm, corresponding either to the size of individual particles (e.g. micelles, microemulsion droplets) or to the range of interaction between particles (e.g. charged polymer latices at low ionic strength). These dimensions, coupled with the fact that most colloids are light-atom structures in water- or oil- based media, make small-angle neutron scattering (SANS) a technique of choice for their study. This is especially true when the colloid is magnetic (as in ferrofluids); in this case neutron polarization analysis[1] coupled with SANS provides a uniquely powerful tool.

An important feature of colloidal suspensions is that their properties are often dominated by one type of particle, which in turn may have one dominating type of interaction with its neighbours. Such systems may be treated as one-component macrofluids (OCM), for which there are a number of theories to calculate structure for different pair interaction potentials[2]. The most typical colloidal potential is the DLVO[3] or screened Coulomb potential, which for spherical particles of diameter σ takes the form

$$\beta V(x) = \gamma \exp(-kx) / x, \quad x > 1 \quad (1)$$

where $x=r/\sigma$, $\beta=1/k_B T$ and $k=\sigma/\lambda_D$, λ_D being the Debye length in the suspension. The dimens-

ionless coupling constant is given by

$$\gamma = \beta \pi \epsilon_0 \epsilon \sigma \psi_0^2 \exp(k) \quad (2)$$

where ψ_0 is the surface potential and ϵ the dielectric constant of the medium. For $x \ll 1$ a hard-core potential is adopted; this is in fact only a perturbation in the calculation of structure as long as $\beta V(x=1) \gg 1$. The important feature of the potential (1) is that it may be varied at will by the experimentalist, via the parameters ϵ , ψ_0 , k and σ . This experimental control is also true for some of the other potentials considered below.

For dilute systems, the particle diameter has little influence on the structure and there is a crossover to plasma-like behaviour, on a length scale characterized by the ion-sphere diameter, $a = (3/4\pi n)^{1/3}$, where n is the number density. In general, the suspension will be characterized by γ , k and the volume fraction $\eta = \pi n \sigma^3 / 6$; η also controls a cross-over in the dynamics, hydrodynamic effects becoming more important as η increases. The characteristic timescales in colloidal dynamics are generally > 1 ns, so that small-angle neutron spin echo (SANSE) provides an ideal complement to SANS for studying the short-time behaviour with which current theories are mostly concerned. At the other extreme of long-time behaviour, appropriate SANS experiments can access the dynamics. We shall give examples of studies in both regimes.

2. Statics.

For scattering from an isotropic suspension of monodisperse particles interacting through a central potential, the scattered intensity at momentum transfer Q may be written

$$I(Q) = P(Q) \cdot S(Q) \quad (3)$$

where $P(Q) = F^2(Q)$, the square of the particle form factor, and the liquid structure factor $S(Q)$ is related to $g(r)$, the pair correlation function, by

$$S(Q) = 1 + h_o(Q) \quad (4)$$

Here, $h(r) = g(r) - 1$ and $h_o(Q)$ is its zeroth order Hankel (Fourier) transform.

Charged micelles (self-assemblies of partly polar, partly non-polar, or "surfactant" molecules) generally interact through a potential of the form (1), which leads to the general form of scattering shown in Fig. 1. At small Q , the repulsive potential lowers the osmotic compressibility [and hence $S(0)$], while at high Q scattering is dominated by single particle geometry. The scattering is well described by eq (3), with $S(Q)$ calculated from eq (1) using integral equation techniques[4-6]. Analysis of the scattering from many such systems has led to the general picture of a "rough" globular micelle, shown schematically in Fig. 2. In other micellar systems, $V(x)$ may be attractive, while for microemulsions the

correlations may be due to excluded volume alone. In most cases the OCM formalism, coupled with current liquid theories to calculate $S(Q)$, leads to good agreement with experiment[2].

Dipolar interactions have also been studied, using stable colloidal suspensions of spherical magnetic particles (Co , Fe_3O_4) dispersed in either water or oil: ferrofluids. In a saturating magnetic field H the interaction potential takes the form

$$\beta V(x) = \beta V_c(x) - 2(\mu^*)^2 P_2(\hat{H} \cdot \hat{r}_{12}) / x^3 \quad (5)$$

where $V_c(x)$ is the central part of the potential, $\mu^* = \sqrt{(\beta \mu^2 / \sigma^3)}$ and r_{12} is the vector between the centres of particles 1 and 2, each with moment μ ; $\hat{}$ signifies a unit vector. In this case eq (4) becomes

$$S(Q) = 1 + n \sum_1 h_1(Q) F_1(\hat{Q} \cdot \hat{H}) \quad (6)$$

where $h_1(Q)$ is the Hankel transform of order 1. An approximate analytic theory[7] is available to calculate the $h_1(Q)$ for a potential of the form (5); comparison with molecular dynamics shows that the approximation is good provided the density of the ferrofluid is not too low[8]. SANS with polarization analysis has also been used to separate spin-non-flip (snf) coherent scattering from magnetic fluctuation scattering in a dense ferrofluid[9]. As is evident from Fig. 3, the comparison between

theory and experiment is quite good.

3. Dynamics.

An important feature which distinguishes the OCM from a conventional fluid is the presence of a viscous medium between the fluid particles. While this has no effect on structure (except near walls), it can play an important role in the liquid dynamics because of hydrodynamic backflow effects. We first write the dynamical structure factor $S(Q,t)$ as a cumulant expansion:

$$S(Q,t) = S(Q) \exp\{-[v_1(Q)t + v_2(Q)t^2/2 + \dots]\} \quad (7)$$

and note that the collective relaxation frequency $v_1(Q)$ is accessible from an experimental measurement of the normalized dynamic structure factor at short times[10]:

$$v_1(Q) = [\partial \ln S_N(Q,t) / \partial t]_{t=0} \quad (8)$$

where $S_N(Q,t) = S(Q,t)/S(Q)$; this is the inherently normalized quantity measured by SANSE[11]. A review of the theories used to calculate $v_1(Q)$ has been given by Hess and Klein[12]. In mean-field approximation

$$v_1(Q) = D_{eff}(Q) + nQ \cdot \{D_{12}(r)g(r) \cdot Q \exp(-iQ \cdot r) dr / S(Q)$$

with $D_{eff}(q) = D_0/S(Q)$, where D_0 is the single particle Stokes-Einstein diffusion

coefficient and D_{12} is the distinct part of the diffusion tensor. In the absence of hydrodynamic interactions, the second term in eq (9) vanishes, leaving the remarkable result that the collective relaxation is determined by the static correlations. In dilute charged colloids, the DLVO interaction appears to dominate hydrodynamic effects. An example is given in Fig. 4a, which shows $D_o/D_{o,++}(Q)$ measured by SANSE compared with $S(Q)$ derived from static SANS data. Since all quantities are dimensionless, no fitting is involved and the agreement is very good. At higher concentration (Fig. 4b), the agreement is markedly worse, due to the stronger hydrodynamic coupling. The dashed line uses an *ansatz* to include some hydrodynamic correction[6], but a rigorous calculation is at present unavailable.

SANS may also be used to study the hydrodynamics of colloidal systems when the relaxation times become long enough. One technique is to subject the sample to a viscous shear, G , and measure the scattering, from which the rotational diffusion coefficient, D_r , may be determined[13]. Fig. 5 shows typical data from a suspension of cylindrical micelles having diameter 5 nm and length 320 nm. In the usual (θ, ϕ) polar coordinates, the particle orientation in the viscous shear field is well described here by a normalized orientational probability function

$$p(\theta, \phi; \Gamma) = \frac{(1 - \cos 2\phi_0)(1 + \sin^2\theta \cos 2\phi_0)^{3/2}}{4\pi[1 - \sin^2\theta \cos 2\phi_0 \cos 2(\phi - \phi_0)]^2}$$

where $\Gamma = G/D_r$ and $2\phi_0 = \arctan(8/\Gamma)$. For the system of Fig.5, D_r is found to be 390 s^{-1} . Much longer relaxation times may be found in other systems, and real-time relaxation has been observed using time-sliced SANS after a sudden transition to $G=0$ [14].

4. Conclusion.

The spatial and temporal correlations in colloidal systems are well-suited to SANS and SANSE studies. These studies have provided confirmation of many aspects of current structural theories of complex fluids, and they are beginning to give some insight into the hydrodynamic interactions in such systems.

Acknowledgements.

This research was partially sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. Experiments were performed at Institut Laue-Langevin, Grenoble, France and at the National Center for Small-Angle Scattering Research (NCSASR), Oak Ridge. NCSASR is funded by National Science Foundation Grant #DMR-77-244-58 through Interagency Agreement #40-637-77 with the Department of Energy.

References.

- [1] R.M. Moon, T. Riste and W.C. Koehler,
Phys. Rev. 181 (1969) 920.
- [2] J.B. Hayter, Faraday Discuss. Chem. Soc.
76 (1983) 7.
- [3] E.J.W. Verwey and J.Th. Overbeek, Theory
of the Stability of Lyophobic Colloids
(Elsevier, Amsterdam, 1948).
- [4] J.B. Hayter and J. Penfold, Colloid
Polymer Sci. 261 (1983) 1022.
- [5] J.P. Hansen and J. Hayter, Molec. Phys.
46 (1982) 651.
- [6] J.B. Hayter and J. Penfold, J. Chem.
Soc., Faraday Trans. I, 77 (1981) 1851.
- [7] J.B. Hayter and R. Pynn, Phys. Rev.
Lett., 49 (1982) 1103.
- [8] S. Hess, J.B. Hayter and R. Pynn, Molec.
Phys., 53 (1984) 1527.
- [9] R. Pynn, J.B. Hayter and S.W. Charles,
Phys. Rev. Lett., 51 (1983) 710.
- [10] P.N. Pusey, J. Phys. A, 8 (1975) 1433.
- [11] For details of SANSE see: Neutron Spin
Echo, F. Mezei, ed. (Springer-Verlag,
New York, 1980).
- [12] W. Hess and R. Klein, Physica A, 99
(1979) 463.
- [13] J.B. Hayter and J. Penfold, J. Phys.
Chem., 88 (1984) 4589.
- [14] L. Herbst, H. Hoffmann, J. Kalus, H.
Thurn and K. Ibel, IAEA Report CN-46/IP,
(IAEA, Vienna, 1985).

Captions for figures.

Fig.1. Measured (●) SANS intensity for 0.03M hexadecyltrimethylammonium chloride in D₂O at 313K. Lines correspond to eq (3).

Fig. 2. "Rough" micelle formed from sodium octanoate in water. R_1 is the radius of the largest sphere not containing a polar head, and R_2 is the radius of the smallest sphere containing the entire micelle.

Fig. 3. Measured coherent snf and fluctuation scattering from a concentrated ferrofluid at applied field (a) $H=0.5T$, (b) $H=0.2T$. Approximate theory (---); theory corrected for truncation effects (—)[9].

Fig. 4. Dimensionless comparison of static and dynamic scattering data from (a) 0.1M, (b) 0.4M sodium dodecyl sulfate in D₂O at 303K[6]. Calculated lines are discussed in the text.

Fig. 5. Two-dimensional SANS intensity from 0.03M hexadecyltrimethylammonium bromide in 0.4M KBr at 313K under applied shear rates $G = \partial v_x / \partial y = 1000 \text{ s}^{-1}$ (a) and 3800 s^{-1} (b). Black corresponds to maximum, white to zero intensity; Q-range is $\pm 0.8 \text{ nm}^{-1}$ in x and z .