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SCATTERING FROM CORRELATIONS IN COLLOIDAL SYSTEMS

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INTRODUCTION

Colloidal suspensions typically exhibit spatial correlations over distances of order 10^{-10} to 10^4 Å, corresponding either to the size of individual particles (e.g. polymer chains, surfactant micelles) or to the range of interaction between particles (e.g. charged polymer lattices at low ionic strength). Apart from having fundamental intrinsic interest, such systems are also extremely useful as model systems with which to study, for example, non-Newtonian hydrodynamics, since temporal correlations are generally much longer lived (10^{-8} to 10^{-3} sec) than those found in simple atomic or small molecular systems (10^{-13} to 10^{-10} sec). Colloids have long been the subject of macroscopic phenomenological research (on rheological properties, for example), but it is only recently that microscopic light, x-ray and neutron scattering techniques have been applied to their study, in large part because of theoretical difficulties in understanding the scattering from dense liquid-like systems of interacting particles. For spherical colloids, such theoretical problems have now been largely overcome¹, and for anisotropic colloids experimental techniques are being developed which circumvent the intractable theoretical areas². This paper will first review some static light and small-angle neutron scattering (SANS) results on colloidal suspensions, both at equilibrium and in steady-state non-equilibrium situations, and will then discuss some dynamic measurements on polymer solutions and melts made using the neutron spin-echo (NSE) technique. Emphasis is placed on experiments which have a possible counterpart in synchrotron radiation studies. In particular, NSE extends the results of photon correlation spectroscopy (PCS) to larger momentum transfers and shorter time-scales than are available with visible light, and the extension of PCS to short wavelength on a synchrotron source would be of similar fundamental interest.

STATIC STRUCTURE

A number of examples of measuring individual particle structure by SANS has been given in the article by Dr. George Wignall (this symposium). Here, we shall restrict discussion to suspensions in which the particles interact with one another. The general statistical-mechanical problem associated with describing the structure of a concentrated colloidal dispersion is to predict the properties of the dispersion, given the structure and laws of interaction of all the particles of which it is composed. Thus formulated, the direct theoretical problem is at present intractable. We may, however, pose a more tractable problem by concentrating on the component of most interest, namely the colloidal particles themselves.

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MASTER

To set this approach on a quantitative basis, consider a scattering experiment designed to measure the structure of a concentrated colloidal dispersion. Radiation (light, X-ray or neutron) of momentum k_i impinges on a sample and is scattered through angle 2θ with final momentum k_f . The experiment performed is to measure the scattered intensity $I(Q)$ as a function of the momentum transfer $Q = k_i - k_f$; for elastic scattering $|Q| = (4\pi/\lambda)\sin \theta$. Each atom in the suspension has an associated scattering amplitude b , where b depends on the nuclear type and electronic moment of the atom for neutrons, and on electron density for electromagnetic radiation. The scattered intensity is thus calculated by summing all the scattered waves, taking into account amplitudes due to scattering type and phase shifts due to scattering position, and averaging the result over all possible configurations weighted by their probability of occurrence:

$$\begin{aligned}
 I(Q) &= \langle |\sum_j b_j \exp(iQ \cdot R_j)|^2 \rangle \\
 &= \langle \sum_{jk} b_j b_k \exp[iQ \cdot (R_j - R_k)] \rangle
 \end{aligned}
 \tag{1}$$

where R_j is the position of the j th atom, the sum is over all atoms in the suspension and $\langle \rangle$ indicates taking the ensemble average. It is the calculation of this latter average which poses the central (and generally unsolved) statistical-mechanical problem.

The approach which has proved most successful is to consider the colloidal particles to be the only finite objects present in the suspension, all other ions and the solvent merely forming a neutralizing background. The problem is then reduced to calculating the scattering from a one-component macrofluid (OCM) interacting through a specified pair potential. For the OCM we may immediately exclude all atoms other than those in the colloidal particles from the summation, and we may further split the sum into a sum with j and k both in the same particle, plus a sum over j and k belonging to different particles. On the further assumption that the particles are independently oriented, the result is³

$$I(Q) = S(Q) \langle F(Q) \rangle_Q^2 + \langle F^2(Q) \rangle_Q - \langle F(Q) \rangle_Q^2
 \tag{2}$$

where

$$F(Q) = \sum_j b_j \exp(iQ \cdot r_j)$$

is the single-particle form-factor (the sum running over all distances r_j within a particle relative to the particle centre) and $\langle \rangle_Q$ indicates an angular average over all orientations of the particle with respect to the direction of Q . Here we have assumed the particles are monodisperse for simplicity.

The interparticle structure factor $S(Q)$ specifies the correlations between the centres of different particles. While $F(Q)$ and the related angular averages can be calculated easily (although perhaps numerically) for any given particle model, the calculation of $S(Q)$ requires the evaluation of an ensemble average over all particle configurations:

$$S(Q) = 1 + \rho \langle \sum_{n \neq m} \exp(iQ \cdot R_{mn}) \rangle \quad (3)$$

where ρ is the number density of particles in the suspension and R_{mn} is the distance between the centres of particles m and n . It is important to note at this point that, in reducing the problem to one for which solutions may be found, we have already made two strongly restrictive assumptions: particles are monodisperse and they are independently oriented. While polydispersity can be introduced in certain cases, there is no way at present to handle the general problem of correlated orientations of non-spherical particles in a way which is useful to the experimentalist; however, experimental techniques are available which sidestep this problem by imposing total correlation of orientation.

Typical results of using the OCM procedure to interpret experiments on charged polymer lattices are shown in Fig. 1. Here, the interactions are of

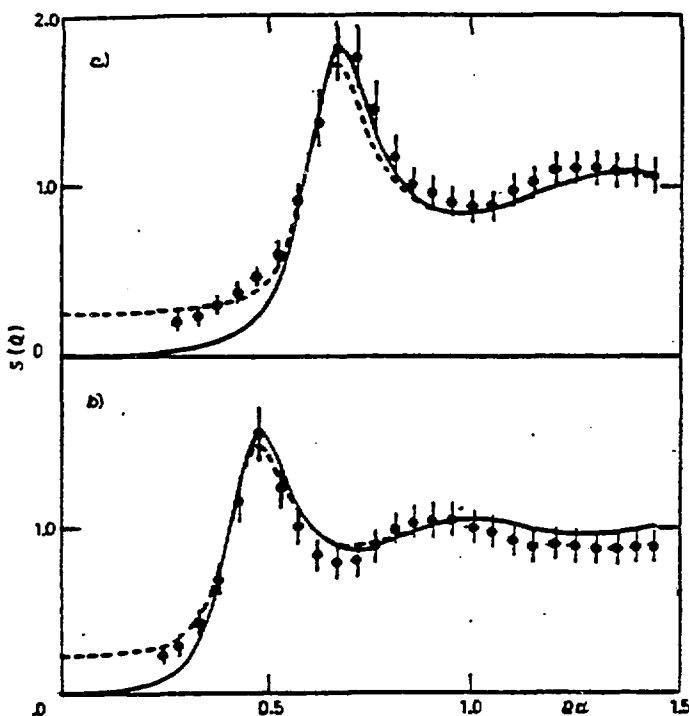


Fig. 1. Light scattering data⁴ from charged polystyrene spheres of diameter d at volume fractions of (a) 4.8×10^{-4} , (b) 1.7×10^{-4} . Solid lines are calculated^{5,6} on a monodisperse OCM model, dashed lines include polydispersity.

the repulsive screened Coulomb type. The same approach has been used to account for critical scattering on approaching a phase transition in a non-ionic micellar system with attractive interactions⁷.

An interesting example of the OCM approach being applied to a system with anisotropic interactions is provided by magnetic colloids, or ferrofluids. In this case, a saturating magnetic field may be applied to align all dipoles parallel to the field, and the theoretical calculation of

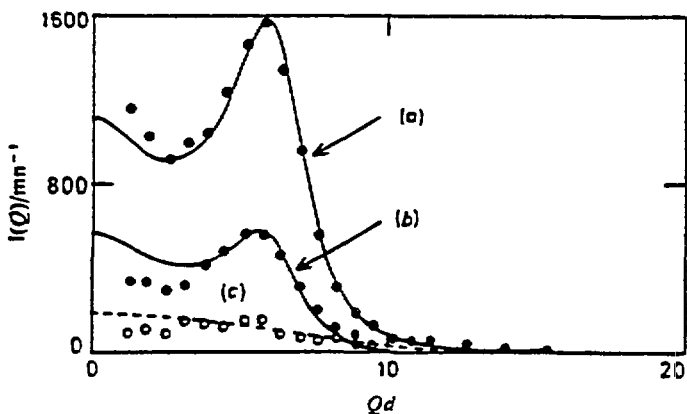


Fig. 2. Comparison of experiment (●) with theory (-) for scattering from a concentrated cobalt ferrofluid in a field of 0.5 T.

(a) Magnetic plus nuclear scattering
 (b) nuclear scattering
 (c) magnetic fluctuation scattering.

correlations in the fluid becomes feasible⁸. Fig. 2 shows that the agreement with experiment is excellent⁹. In this case, neutrons have an advantage over electromagnetic radiation because the large magnetic cross-section allows easy application of polarization analysis techniques¹⁰.

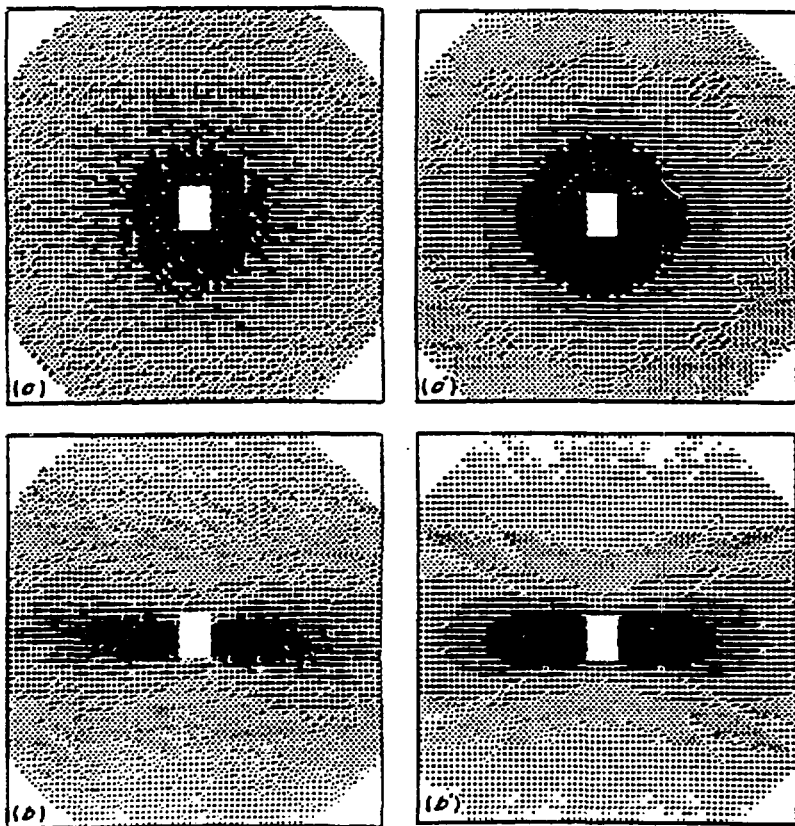


Fig. 3. Measured (a,b) and calculated (a',b') scattered intensity maps for shear-aligned cylindrical micelles. (a,a') static; (b,b') shear gradient = 7500 s⁻¹. The Q-range is ±0.048 Å⁻¹ in both dimensions.

STEADY-STATE NON-EQUILIBRIUM STRUCTURE

The factorization of eq. (1) becomes intractable for anisotropic colloids, where correlations may develop between the relative orientations and positions of the particles. In the previous section, application of a magnetic field provided one technique for overcoming this problem in a magnetic system. In some non-magnetic systems, the application of a viscous shear may similarly be used to align the particles for study by scattering techniques. Fig. 3 shows typical results obtained on a solution of cylindrical micelles of diameter 50Å and length 3200Å, together with the corresponding absolutely scaled theory². These types of experiment, as well as allowing a clear understanding of the colloidal system under study, provide models for studying shear induced melting and ordering; both light¹¹ and neutron scattering¹² have been used. From the point of view of synchrotron experiments, sheared systems have the useful added feature of providing an obvious way to overcome local heating effects in the solution when focussed beams are employed, for example to illuminate only a few particles in studies of multipoint correlation functions¹³.

DYNAMIC STUDIES OF POLYMERS AND COLLOIDS

Photon correlation spectroscopy has proved an extremely useful technique for studying relaxation phenomena in colloidal systems¹⁴. As typically applied with visible light sources, however, PCS is limited to momentum transfers $Q < 10^{-3} \text{ \AA}^{-1}$; it is thus suited to observations of the motion of an entire polymer coil, for example, but is unable to provide information on the spatial scale of polymer segmental motion within the chain.

Neutron spin-echo¹⁵ provides a complementary technique which measures the same physical quantity as PCS, namely the normalized coherent time correlation function $F_N(Q,t)$, but at sufficiently large momentum transfers to probe finer spatial scale than the optical technique. The reader is referred to recent reviews^{16,17} for details of the method, and we shall only discuss some representative results in this article.

The description of polymer relaxation in solution, on the scale of segmental diffusion (Flory radius $R_0 > r > \text{segment length } \ell$), is based on the use of hydrodynamic equations; the hydrodynamic interaction between the monomers has to be included to obtain physically realistic predictions. The influence of concentration is treated by introducing a correlation length ξ which corresponds roughly to the distance between entanglement points of different polymers; over distances $r < \xi$, essentially single-chain behaviour should still be observed. In good solvents, ξ scales with concentration as $c^{-3/4}$, and the width of the relaxation spectrum is predicted to scale with Q^3 .

A direct theoretical attack on the problem was undertaken by Dubois-Violette and de Gennes¹⁸, who found

$$F_N(Q,t) = (\Gamma t)^{2/3} \int_0^\infty du \cdot \exp \{ -(\Gamma t)^{2/3} u [1 + h(u)] \} \quad (4)$$

where

$$h(u) = \frac{4}{\pi} \int \frac{dy}{y^3} \cdot \cos y^2 [1 - \exp(-y^3 u^{-3/2})] \quad (5)$$

The relaxation frequency Γ is given by

$$\Gamma = \frac{1}{6\pi\sqrt{2}} \cdot \frac{k_B T}{\eta} \cdot Q^3 \quad (6)$$

where η is the solvent viscosity. This result is interesting because it predicts a universal function for all polymers, Γ scaling with Q^3 and depending only on the bulk solvent parameter T/η . Similar results are also predicted in an extended theory due to Akcasu et al.¹⁹ The Q^3 behaviour is expected in the range $QR > 1 > Q\ell$, where R is the radius of gyration and ℓ is of order the monomer size; that is, neither overall molecular size nor detailed local structure dominate.

Spin echo results on dilute solutions of a number of polymers have confirmed the general correctness of this approach^{20,21}, which is basically the Zimm model. Crossover behaviour to Q^2 has also been observed, either due to the onset of entanglement²⁰ (see Fig. 4) or to reduction in molecular weight so that the diffusion of the entire coil is observed²². Both rings and chains have been studied.

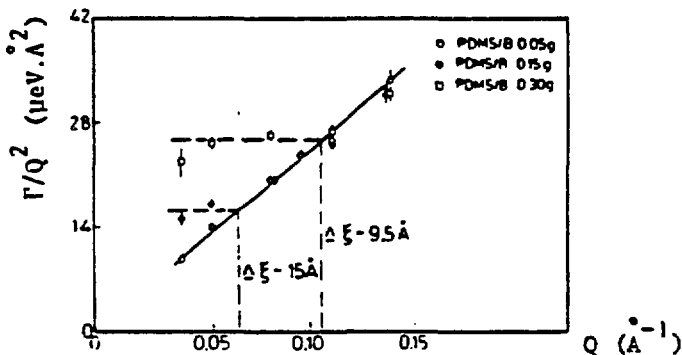


Fig. 4. NSE results²⁰ on PDMS in C_6D_6 , showing the crossover from Q^3 to Q^2 behaviour as the concentration is increased from 5 to 30%. At higher concentration the correlation length, ξ , at which entanglement sets in becomes shorter.

In polymer melts, collective fluctuations appear to vary in accordance with the Rouse model, with the relaxation frequency varying as Q^4 . In this type of neutron scattering experiment, the ability to mark a few chains by using a dilute solution of protonated in deuterated polymer is primordial in allowing the motion of a single chain to be studied. Figure 5, which shows data on polytetrahydrofuran (PTHF), demonstrates the difference between solution and melt dynamics²².

The time-dependence of the relaxation processes in the melt is at variance with the predictions of reptation theory, in which the flexible polymer chain is thought to move snake-like in a "tube" formed by local topological constraints. Figure 6 shows experimental NSE data, together with Monte Carlo simulation results, on a dimensionless plot, compared with the predictions of Rouse and reptation models²³. The Rouse model, which is independent of Q in this format, clearly gives the better description.

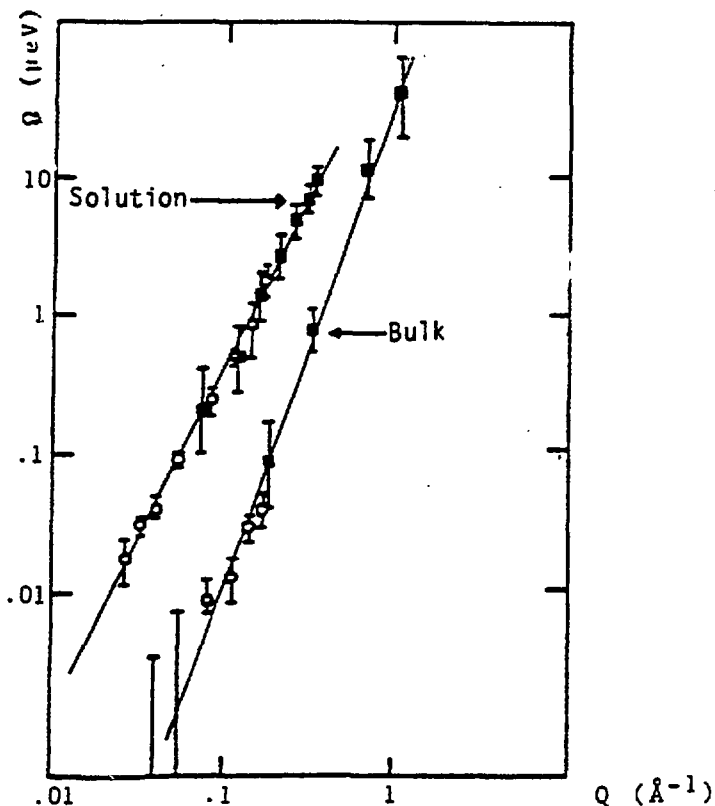


Fig. 5. Variation of relaxation frequency Ω (expressed in energy units) with Q for a 3% solution of PTHF/ CS_2 ($T = 30^\circ C$) compared with a melt sample of 3% PTHF/PTDF ($T = 110^\circ C$). Both backscattering (\blacksquare) and NSE (\circ) data are shown. Note that energies of order 10 neV may be routinely measured with NSE.

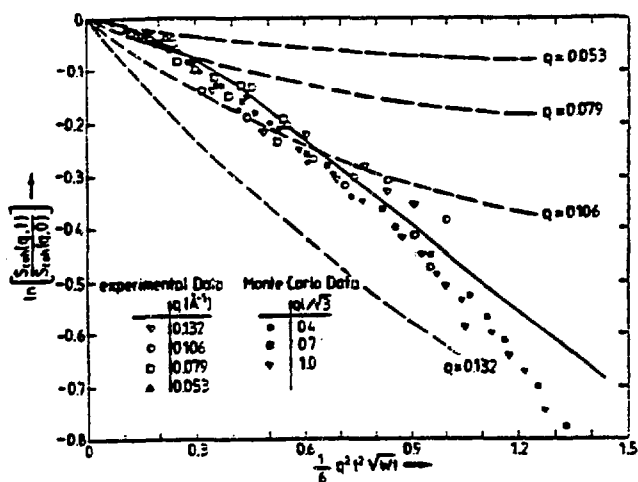


Fig. 6. Normalized time correlation function plotted as a function of $q^2 \lambda^2 (Wt)^{1/2}$, where q is the momentum transfer and W a rate constant²³. — Rouse model; - - - reptation model.

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However, the same model fails to describe the viscosity of the same melts, and the detailed microscopic behaviour in the melt still needs clarification.

A number of other systems has been studied by NSE, including hydrodynamic effects in charged micellar solutions²⁴ and microemulsions²⁵, screening effects in polyelectrolyte behaviour²⁶ and the Q-dependent temperature cross-over in the dynamics of dilute polymer solutions on changing from theta to good solvent conditions²⁷. All of these studies rely on the ability to extend the range of PCS measurements to higher Q by using shorter wavelengths, and the implementation of an equivalent technique at a synchrotron radiation source provides an exciting challenge.

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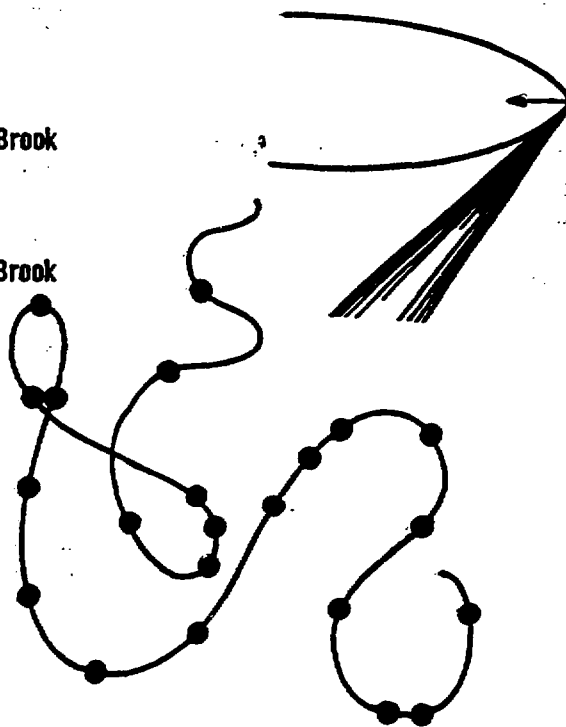
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