Ordered Macromolecular Structures in Ferrofluid Mixtures

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We have observed ordering of dilute dispersions of spherical and cylindrical macromolecules in magnetized ferrofluids. The order results from structural correlations between macromolecular and ferrofluid particles rather than from macroscopic magnetostatic effects. We have aligned elongated macromolecules by this technique and have obtained anisotropic neutron-diffraction patterns, which reflect the internal structure of the macromolecules. The method provides a tool for orienting suspended macromolecular assemblies which are not amenable to conventional alignment techniques.

A wide range of structural possibilities exists when magnetic and nonmagnetic particles coexist in the same colloidal dispersion. For example, a single layer of micron-sized, nonmagnetic spheres suspended in a magnetic colloid, or ferrofluid, [1] may be ordered by the application of a small magnetic field. [2] In this case, the spheres displace ferrofluid and behave in the external field as magnetic holes, with aligned effective moments equal in magnitude to the total moment of ferrofluid displaced. Magnetic interactions between these large effective moments produce chainlike aggregates or 2D crystals, depending on the field direction. When the volume of a nonmagnetic particle is comparable to the mean volume occupied by a ferrofluid particle, however, the concept of an effective moment for the nonmagnetic species is no longer valid, and the system models a novel binary liquid in which dipole-dipole and central interactions coexist. In this Letter, we report small-angle neutron-scattering (SANS) measurements in this binary-fluid limit on dispersions of spherical and rodlike macromolecular assemblies in ferrofluids. By varying the contrasts between the refractive indices of dispersed particles and the carrier fluid, we are able to identify separately the correlations between distinct and similar particles, and to show that anisotropic correlations develop between magnetic and nonmagnetic species in a modest magnetic field. A consequence of this type of cross correlation is that anisotropic, nonmagnetic macromolecules may be easily oriented in dilute ferrofluid suspensions. The latter result provides a new technique for orienting suspended particles, such as biopolymers, which are not amenable to conventional high-field or shear alignment. Application of this method to scattering experiments eliminates partially (or, in favorable cases such as certain viruses, fully) the loss of structural information usually inherent in orientational averaging of the molecular form factor.

The ferrofluids used in these studies are stable suspensions of small (≈ 10 nm diam), approximately spherical, superparamagnetic particles dispersed in water. The ferrofluid magnetization, which is proportional to the volume fraction of magnetic material η_{mag}, reaches a typical saturation value of 50 mT in applied fields of order 10^5 A m^{-1}. In a pure ferrofluid, the anisotropy of correlations between particles of diameter σ_1 and dipole moment μ_1 is controlled by their dimensionless reduced moment μ_1^* defined as $(\mu_1^*)^2 \equiv (\mu_0/4\pi)\mu_1^2/k_B T \sigma_1^3$. (Throughout this paper, subscript 1 will refer to the ferrofluid, and subscript 2 to the nonmagnetic particles.) For practical ferrofluid densities (total volume fraction $\eta_1 \lesssim 0.3$), anisotropic correlations develop[3] between ferrofluid particles for $(\mu_1^*)^2 \gtrsim 1$. If the ferrofluid can be regarded as a continuum, correlations between dispersed nonmagnetic spheres of diameter σ_2 are determined by the effective moment

$$(\mu_2^*)^2 \equiv (\mu_0/4\pi)\delta_{12}^2\mu_1^2/k_B T \sigma_2^3,$$

where $\delta_{12} = (\sigma_2/\sigma_1)^3\eta_1$ is the number of ferrofluid particles displaced by each nonmagnetic particle. This mean-field situation is realized for micron-sized spheres[2] because $(\mu_2^*)^2 \approx 10^3$ at magnetic saturation, whereas $(\mu_1^*)^2 \approx 1$. This description breaks down for the systems we shall discuss because the nonmagnetic macromolecules displace less than one ferrofluid particle ($\delta_{12} < 1$), and so macroscopic magnetostatic arguments do not predict ordering or orientation of the nonmagnetic species. Instead, the system must be regarded as a binary mixture of colloidal particles, in which the carrier fluid plays no role other than to mediate the interparticle interactions.

An expression for the scattering from a binary fluid on nonmagnetic spheres has been given by Ashcroft and Langreth.[4] The extension to neutron scattering by a mixture containing a magnetic species follows the analysis of Moon, Riste, and Koehler.[5] In the presence of a saturating field **H** the scattering at wave vector **q**, for an unpolarized neutron beam, is found to be

$$I(\mathbf{q}) = x[F_{1N}^2(q) + F_{1M}^2(q)\sin^2\psi]S_{11}(\mathbf{q}) + 2[x(1-x)]^{1/2}f_{1N}(q)F_2(q)S_{12}(\mathbf{q}) + (1-x)F_2^2(q)S_{22}(\mathbf{q}), \tag{1}$$

where ψ is the angle between **q** and **H**. In Eq. (1), S_{ij} is the partial structure factor for correlations between particles of types i and j, and $x = n_2/(n_1 + n_2)$, where n_i is the number density of particles of type i with form factor $F_i(q)$: in the case of the magnetic particles, the latter consists of a magnetic part $F_{1m}(q)$ and a nonmagnetic part $F_{1N}(q)$. We note in passing that the terms in Eq. (1) may be measured independently by making use of neutron-polarization analysis.[5,6] However, for these experiments it has proved practical to use the technique of refractive index matching to obtain an appropriate partial separation of the terms in this equation.

SANS measurements were undertaken at the Institut Laue-Langevin, Grenoble, France, at the National Center for Small Angle Scattering Research, Oak Ridge, and at The Neutron Source at the National Laboratory for High Energy Physics (KENS), Japan. In a first series of experiments, polystyrene (PS) latex spheres were added to well-characterized, water-based ferrofluids (FF) in which the refractive indices were varied by using deuterated surfactant in D_2O carrier (DFF), or protonated surfactant in H_2O carrier (HFF). All particle dimensions were determined by SANS measurements of dilute solutions. The FF particles were found to have a mean magnetic diameter $\sigma_{1M} = 20$ nm and mean total diameter $\sigma_1 = 29$ nm, with about 30% polydispersity; for the essentially monodisperse PS, $\sigma_2 = 30 \pm 1$ nm. Scattering experiments were performed on mixtures at volume fractions $\eta_2 = 0.050$ of PS and $\eta_1 = 0.041$ of FF, and on blanks of pure PS ($\eta = 0.05$) or of pure FF ($\eta = 0.041$). Data with the FF blank scattering subtracted are shown in Fig. 1. Model calculations[7] show that subtraction of the blank in this case essentially corresponds to removing the first term in Eq. (1), so that the difference may have either sign, depending on the magnitude of S_{12}, which oscillates about zero. Because of the refractive index matching in the DFF mixture, $F_1(q)$ is small and the scattering is dominated by the last term in Eq. (1). We observe no anisotropy (i.e., ψ dependence) in these data [see Fig. 1(a)], and the q dependence is similar to that of PS in D_2O at the same volume fraction. Thus, the correlations between PS particles are isotropic, even though those between the FF particles are not.[8] For PS in HFF, all terms in Eq. (1) contribute to the scattering, but since we know from the measurements in DFF that S_{22} is isotropic, the anisotropy in the blank-subtracted HFF data shown in Fig. 1(b) must result from the second term in Eq. (1); that is, from anisotropic correlations between nonmagnetic and magnetic particles.

In the second series of experiments, we explored the case of mixtures in which the nonmagnetic particles were essentially rodlike, with aspect ratio of order 10:1. Experiments were performed using well-characterized samples of tobacco mosaic virus (TMV) and tobacco rattle virus (TRV), both of which are cylindrical. In these experiments, the FF selected was first shown by electron microscopy not to cause deterioration of the viruses, which is an important requirement if the technique is to be used for studies of viral structure.

TMV is a hollow cylindrical assembly of length 300 nm, external diameter 18 nm, and internal diameter 4 nm. This virus is exceptional in that it is obtainable in relatively large quantities, and at sufficiently high concentration ($\eta_2 > 0.1$) it forms a nematic liquid-crystalline phase[9] which may be oriented easily by a magnetic field or by hydrodynamic shear. X-ray fiber diffraction data have provided a complete 3D structure at 0.36-nm resolution.[10] A particular feature of the x-ray diffraction patterns is a series of layer lines corresponding to a 6.9-nm periodicity along the rod axis, with extremely strong diffraction every third line reflecting the 2.3-nm pitch of the helix formed by the coat protein subunits.

SANS experiments were performed on TMV dispersed in DFF or HFF at 0.06 volume fraction. The neutron scattering from TMV in DFF at zero field is iso-
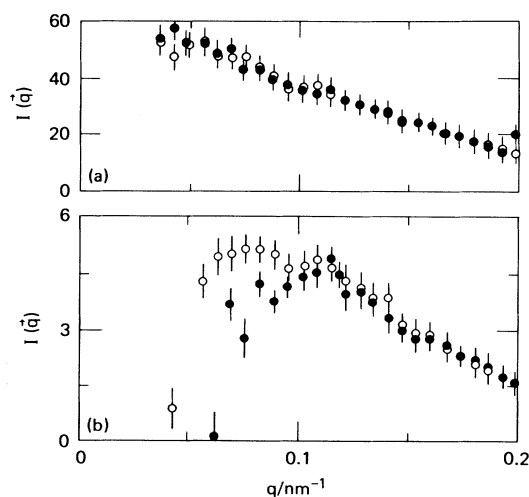

FIG. 1. Blank-subtracted SANS intensity scattered parallel (O) and perpendicular (●) to an applied field $H = 0.3$ T by 0.05 volume fraction of PS in (a) DFF and (b) HFF.
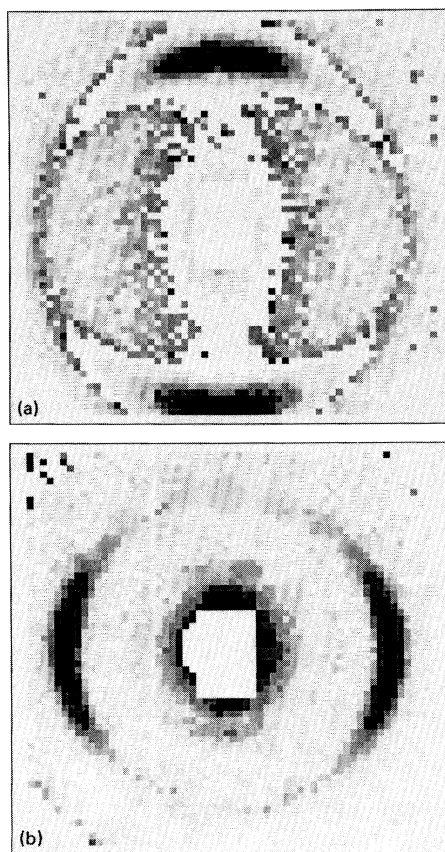
FIG. 2. Blank-subtracted SANS intensity patterns for TMV in DFF at 0.06 volume fraction in a horizontal field $H = 0.5$ T. The vertical and horizontal dimensions of the plot each correspond to $2q_{max}$ momentum transfer, where (a) $q_{max} = 0.20$ nm^{-1} and (b) $q_{max} = 3.55$ nm^{-1}. White corresponds to minimum and black to maximum intensity.
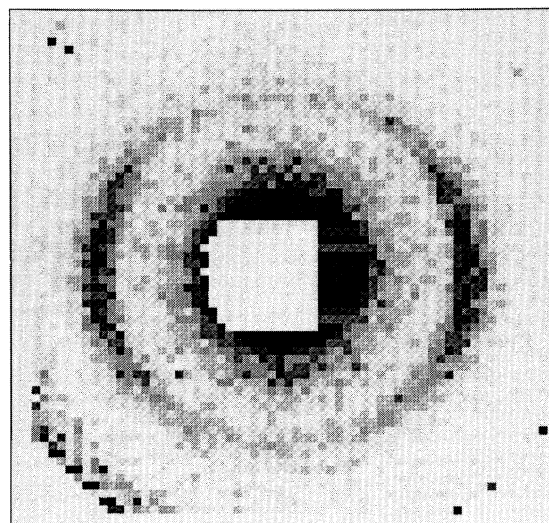

FIG. 3. Blank-subtracted SANS intensity patterns for TRV in DFF at 0.06 volume fraction in a horizontal field $H = 0.5$ T, $q_{max} = 3.55$ nm^{-1}.

tropic, and displays a peak at $q = 2\pi/36.3 = 0.173$ nm^{-1}. This peak is characteristic of correlations between TMV particles $S_{22}(q)$ which result from electrostatic interactions under the solution conditions used. The position of the peak depends on the range of the electrostatic interparticle potential, and thus depends on the pH and ionic strength of the dispersing medium. In a modest applied field ($H = 0.3$ T), the scattering becomes anisotropic, and the peak in $S_{22}(\mathbf{q})$ appears only for $\mathbf{q}$ *perpendicular* to H, as shown in Fig. 2(a). Even though the concentration lies well inside the known isotropic phase boundary for aqueous suspensions of TMV,[9] the viruses have ordered into a nematic structure. This alignment cannot be explained on the basis of magnetostatic arguments because each virus displaces, on average, less than one FF particle. The effect is therefore due to cross correlations of the type described above for isotropic macromolecules.

At larger q, $S_{22}(\mathbf{q}) \to 1$ and $S_{12}(\mathbf{q}) \to 0$, so that peaks in the diffraction pattern reflect the internal structure of the particles themselves. This is shown in Fig. 2(b), where the higher-q peaks now appear for $\mathbf{q}$ *parallel* to H. These peaks correspond to the 2.3-nm layer lines discussed above. The alignment of the viruses in this phase, determined from the resolution-corrected angular width of the diffraction peaks ($\Delta\psi = 19°$ HWHM) corresponds to a nematic order parameter of ≈ 0.8. Even in this highly favorable material, conventional magnetic alignment techniques are unable to produce this degree of order below volume fractions of 0.12.[9]

Many biological structures have neither sufficient diamagnetic anisotropy to allow orientation in an intense magnetic field, nor appropriate electrostatic or morphological characteristics to respond to shear alignment. For example, TRV, which is genetically unrelated but morphologically similar to TMV, shows only poor orientation under shear, and we were unable to align it magnetically in a 7-T field, even at the high concentration of 100 mg/ml. However, when TRV is ferrodispersed in DFF at a volume fraction of 0.06, a field of 0.5 T is sufficient to produce the high-q diffraction pattern shown in Fig. 3. This pattern, which has a degree of alignment comparable with that obtained for the TMV, shows layer lines corresponding to a 2.5-nm repeat distance along the rod.

In conclusion, we have demonstrated the importance of cross correlations in determining structural order in dilute suspensions of mixed magnetic and nonmagnetic colloidal particles, and have shown that these effects may be used to align anisotropic macromolecules for diffraction studies. We believe that this technique of ferrodispersion will be useful for ordering a variety of colloidal particles in suspension, and may have interesting

possibilities for submicron engineering in general, especially when combined with field gradient techniques. The ability to work with low concentrations makes the method of particular interest for aligning biological materials, such a chromatin, which are not easily obtainable in quantity.

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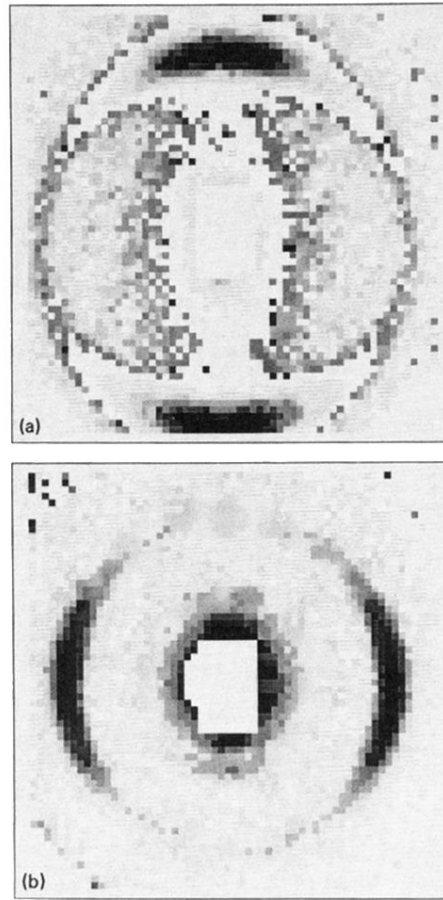[10]K. Namba and G. Stubbs, Science **231**, 1401 (1986).

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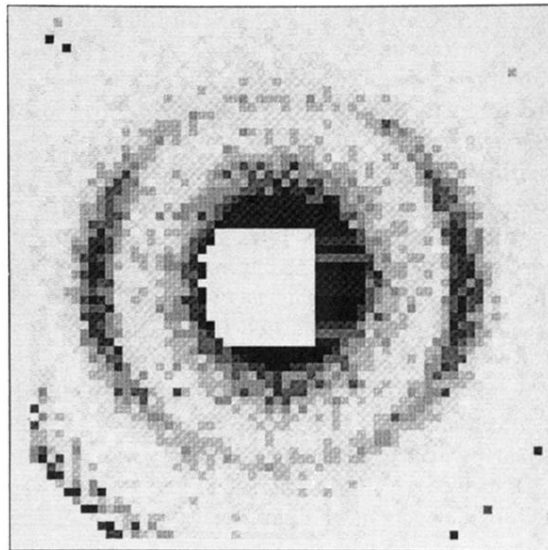
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