cies, the impurity excitations are delocalized or extended throughout the solvent. This behavior, illustrated in Fig. 2, is analogous to the familiar phenomenon of impurity vibrational states in simple crystals. Indeed, for each translational configuration of the atoms, the coupled Drude oscillators, used here to mimic the quantum electronic degrees of freedom in a liquid, can be viewed as a harmonic system.

The variation between localized and extended impurity states could be observed experimentally in a single system through the application of high pressure to vary density. Changes in density will alter the impurity resonance frequency and the band frequencies, thus enabling one to move between various cases illustrated in Fig. 2. Note also the possibility of intense resonances for special choices of the parameters characterizing the system. A variety of physical and chemical systems should exhibit this type of phenomena, and it is significant that one can describe it within the framework of an analytically solvable model of a fluid. Further, as discussed in Refs. 1 and 2, the model can be readily extended both from a mean-field theory and from the idealized Hamiltonian of point Drude oscillators embedded in hard spheres. The possibility of such extensions is encouraging for possible applications in the future.

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Structure Factor of a Magnetically Saturated Ferrofluid

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An analytic form for the structure factor of a fully aligned ferrofluid is presented. This model consists of spherical colloidal particles interacting through magnetic dipolar and attractive central potentials. The main feature of the method is the reduction of the problem to that of calculating the correlations in an isotropic fluid with the central interaction in rescaled form. The results show the particle chaining first proposed by de Gennes and Pincus.

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The intrinsic physical interest and technological importance of ferrofluids has led to a dramatic recent increase in the number of publications and patents involving these materials.[1] Although de Gennes and Pincus[2] conjectured a decade ago that such fluids would contain chains of particles which could be aligned by an applied magnetic field, $\vec{H}$, we know of no formal calculation of interparticle correlations which shows this effect for an aligned system. Recent neutron small-angle scattering experiments[3] which show strong anisotropy of the diffraction pattern in the presence of an applied field have emphasized the need for a framework in which to analyze data. We present in this Letter an analytic form for the liquid structure factor $S(\vec{q})$ for a ferrofluid aligned by a saturating magnetic field. Insofar as our method provides a simple prescription for calculating the static structure of an aligned fluid it may yield insight into the behavior of other aligned systems such as liquid crystals.

The model ferrofluid[2,4] we consider consists of monodisperse, spherical, ferromagnetic particles each covered by a nonmagnetic molecular coating, in colloidal suspension. Typically[3,4] the magnetic core comprises ~10% of the total volume of the particle whose overall diameter $\sigma \sim 10^2-10^3$ Å. The spherical symmetry ensures that the magnetization may be represented by a permanent dipole of moment μ situated at the center of each particle. Thus the interaction between particles consists of central Van der Waals and hard-core potentials plus a long-range dipole-dipole interaction. Our present interest is the fully aligned ferrofluid in which thermal fluctuations of the moment direction and local-field effects are negligible. This requires[2] that $\beta\mu H \gg 1$ and $H \gg \mu/\sigma^3$, where $\beta = 1/k_B T$. If the second condition is satisfied, thermal fluctuations may be ignored if the reduced dipole moment[5] μ^* ($\mu^{*2} = \beta\mu^2/\sigma^3$) is of order unity or greater.

We start by expanding the total correlation function $h(1,2)$ of particles labeled 1 and 2 as the series

$$h(1,2) = \textstyle\sum_l h_l(R_{12}) P_l(\cos\theta_{12}), \qquad (1)$$

where P_l is a Legendre polynomial and θ_{12} is the angle between $\vec{H}$ and the vector $\vec{R}_{12}$ joining particles 1 and 2. By symmetry only even values of l appear in Eq. (1). The quantity $h(1,2)$ is related to the direct correlation function $c(1,2)$ by the Ornstein-Zernike (OZ) equation

$$h(1,2) = c(1,2) + \rho \int h(3,2) c(1,3)\, d(3), \qquad (2)$$

where ρ is the particle number density and the integration is over the position of particle 3. Substitution of Eq. (1) and the equivalent expansion of $c(1,2)$ in Eq. (2) yields the hierarchy of equations ($l = 0, 2, \ldots$)

$$h_l(q) = c_l(q) + \rho \textstyle\sum_{mn} h_m(q) c_n(q) |C(mnl;00)|^2, \qquad (3)$$

where $h_l(q)$ and $c_l(q)$ are Hankel transforms

$$h_l(q) = 4\pi(-i)^l \int r^2 j_l(qr) h_l(r)\, dr \qquad (4)$$

and $C(mnl;00)$ is a Clebsch-Gordan coefficient. Derivations of the OZ equation in a form equivalent to Eq. (3) have been given for isotropic fluids by Blum[6] and by Pynn.[7] In terms of $h_l(q)$ the liquid structure factor $S(\vec{q})$ is given by

$$S(\vec{q}) = 1 + \rho \textstyle\sum_l h_l(q) P_l(\cos\varphi), \qquad (5)$$

where φ is the angle between $\vec{q}$ and $\vec{H}$.

To solve the hierarchy of equations (3) an appropriate closure is required. For several reasons we choose to use the mean spherical approximation[8] (MSA). Although this approximation is known to be deficient in predicting thermodynamic properties, it gives excellent results for the static structure of colloidal systems with screened Coulomb interactions.[9] In addition Wertheim[10] has shown that the specific form of the dipole potential allows analytic solution of the MSA equations for an isotropic fluid when these equations are truncated in a physically reasonable manner. The MSA closure relations are, *for* $r > \sigma$,

$$c_0(r) = -\beta V_0(r); \quad c_2(r) = 2\beta\mu^2/r^3; \quad c_l(r) = 0 \text{ for } l > 2, \qquad (6)$$

and for $r < \sigma$,

$$h_0(r) = -1; \quad h_l(r) = 0 \text{ for } l \geq 2, \qquad (7)$$

where $V_0(r)$ is the central part of the interaction between particles.

In his solution for the isotropic dipolar fluid, Wertheim[10] supplemented the MSA closure by the assumption that $h_l(r) = c_l(r) = 0$ for all r and $l > 2$, thereby truncating the hierarchy of OZ equations at $l = 2$. This *Ansatz* gives unreasonable results in the case of an aligned fluid since it predicts that $h_2(q)c_2(q) = 0$. Nevertheless, since we expect h_l and c_l to be small for $l > 2$, we argue that the hierarchy of equations (3) may be truncated at $l = 2$ provided that $h_2(q)$ is replaced by an effective value $\underline{h}_2(q)$. Thus we set all correlation functions with $l > 2$ to zero and write Eq. (3) as

$$h_0(q) = c_0(q) + \rho[h_0(q)c_0(q) + \underline{h}_2(q)c_2(q)/5], \qquad (8)$$

$$\underline{h}_2(q) = c_2(q) + \rho[h_0(q)c_2(q) + \underline{h}_2(q)c_0(q) + 2\underline{h}_2(q)c_2(q)/7]. \qquad (9)$$

If we assume that $\underline{h}_2(q)$ is identical with $h_2(q)$ and solve Eqs. (6) through (9) (see below) we find that $h_2(q)$ is finite at $q = 0$. Equation (5) then implies an unphysical angular behavior for $S(\vec{q})$ at small q. Taking finite sample size into account corrects this result only for $q \lesssim L^{-1}$, where L is a linear dimension of the sample. Since $\underline{h}_2(q)$ and $h_2(q)$ are identical in the limit $\rho \to 0$ we propose to write

$$\underline{h}_2(q) = (1-\gamma)h_2(q) + \gamma h_2^{0}(q)\,, \qquad (10)$$

where $h_2^0(q)$ is the zero-density value of $h_2(q)$, and to chose γ so that $\underline{h}_2(q)$ vanishes at $q=0$.

The detailed solution of Eqs. (6) through (9) will be published elsewhere.[11] Briefly, the transformation

$$\tilde{h}_k(q) = h_0(q) - a_k \underline{h}_2(q)\,, \qquad (11)$$

where $a_1 = 0.326\,6193$ and $a_2 = -1/5a_1$, diagonalizes Eqs. (8) and (9) which then have the form of OZ equations whose closure corresponds to the MSA with rescaled central interactions only. Solutions are known for several forms of the latter, the simplest of which is the hard-sphere interaction $V_0 = 0$. When a Yukawa form of $V_0(r)$ is used to account for the particle "stickiness" the solution of Hayter and Penfold[9] may be used. In either case $\tilde{c}_k(r)$, the Fourier transform of $\tilde{c}_k(q)$, is given by

$$\tilde{c}_k(r) = H_k c(r, \rho H_k, V_0/H_k)\,, \qquad (12)$$

where $c(r, \rho, V_0)$ is the (known) solution of the OZ equation for a fluid of density ρ and interparticle potential $V_0(r)$. The rescaling parameters H_k are given by

$$H_k = 1 - 3a_k\left[(1-\gamma)\int_\sigma^\infty h_2(r) r^{-1}\,dr + 2\gamma\mu^{*2}/3\right], \qquad (13)$$

where the coefficient of a_k in Eq. (13) is determined[10] by solving

$$q_2 - q_1 = 16\eta\mu^{*2}(a_1 - a_2) \qquad (14)$$

with $\eta = \pi\rho\sigma^3/6$ as the volume fraction and

$$q_k = 1 - 4\pi\rho\int_0^\infty r^2 \tilde{c}_k(r)\,dr\,. \qquad (15)$$

The choice of γ discussed above yields $\gamma = 1/q_1 q_2$. The $\tilde{c}_k(q)$ determined by this procedure yield the $h_k(q)$ via the OZ relations and Eqs. (11) and (10), and $S(\vec{q})$ follows from Eq. (5).

In Fig. 1(a) we show the calculated structure factor for $\vec{q}$ perpendicular and parallel to $\vec{H}$, taking a fluid without attractive central interactions to display more clearly the effects of the magnetic dipolar interaction. The dashed lines show the effect of setting $\gamma = 0$ in Eq. (10). Evidently only the small-q region ($q\sigma \lesssim 4$) is influenced by the value of this parameter. The corresponding pair correlation function, $g(\vec{r})$, shows no visible manifestation of the value of γ on the scale of Fig. 1(b). This figure shows several noteworthy features. In the direction parallel to the field, the peaks in $g(r)$ occur at approximate multiples of the particle diameter, indicating the probable presence of a series of neighbors on either side of a given particle. Immediate nearest-neighbor contact is particularly likely. In contrast, perpendicular to the field, such contacts are almost suppressed. The more quickly damped spatial structure in the latter case corresponds more closely to that due to excluded-volume correlations alone. These features, which differ from those found for a similar *isotropic* dipolar fluid,[5] demonstrate the existence of particle chaining in the direction parallel to the applied field. This phenomenon, first suggested by de Gennes and Pincus,[2] has recently been found in molecular dynamics simulations.[12] The main qualitative effect of including particle "stickiness" is to increase the value of $g(\vec{r})$ close to contact.[13]

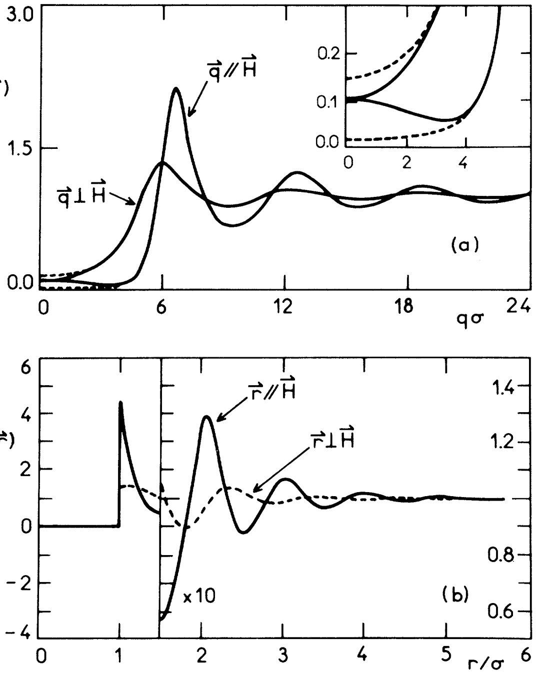

FIG. 1. (a) Calculated structure factors for $\eta = 0.3$ and $\mu^* = \sqrt{3}$. The dashed lines show the corresponding results obtained by direct truncation of the Ornstein-Zernike equations at $l = 2$. (b) Calculated pair correlation functions for $\eta = 0.3$ and $\mu^* = \sqrt{3}$.

We have used the present theory to calculate the neutron scattering cross section for the dilute ferrofluid studied by Cebula, Charles, and Popplewell.[3] Although the agreement with the published data is remarkably good, the comparison does not provide a significant test of our theory, since we find that the scattering from their system is dominated by the magnetic and nuclear form factors of the individual colloidal particles. Our calculations indicate that significant effects due to dipole-dipole correlations should be observed at volume fractions $\eta \gtrsim 0.2$, and thus provide motivation for measurements on denser systems, preferably using neutron polarization analysis to separate magnetic and nuclear scattering.

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Kondo Volume Collapse and the $\gamma \to \alpha$ Transition in Cerium

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The free energy stabilizing the Kondo singlet state is shown to be important in the total-energy and stability conditions for cerium and related solids. Explicit calculations are given for the simplest spin-$\frac{1}{2}$ Kondo model, using the relation to the Anderson Hamiltonian, which leads to a semiquantitative description of the $\gamma \to \alpha$ phase transition in cerium. The temperature dependence of the free energy has a universal form which can lead to a phase boundary terminating in two critical points.

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Cerium is an archetypal narrow-band metal. With temperature and pressure, its electronic and magnetic properties manifest extreme variations that are especially pronounced because of the existence of the first-order isostructural $\gamma \to \alpha$ phase transition ending in a critical point, unique among elemental solids.[1] Extensive studies near the phase boundary, combined with work on γ-like and α-like Ce impurities, alloys, and compounds, have established the causes of these phenomena to be electronic correlations resulting from coupling of localized $4f$ to delocalized band states.[1-3] The difficulty of the resulting many-body problem has led to many proposals based upon different interpretations of experimental data.[1-13] However, because of the magnitude of the volume change (~15%), all explanations of the $\gamma \to \alpha$ transition have required a gross change in the $4f$ electrons: promotion to band states reducing the $4f$ occupation,[4,5] a Mott transition in which the $4f$ states change from localized to bandlike,[6] or transfer of the $4f$ wave function from the inner to the outer well of the double-well atomic potential.[7] On the other hand, experimental probes[6,7,10-14] of the $4f$ electrons have consistently found only small differences between γ- and "collapsed" α-like Ce materials and have indicated near-integral occupation[6,7,10,11,14] and atomiclike form factors[14] and correlation energies[13] in all cases. The many-body problem presented by this information is closely related to the Kondo effect, and it has been shown that the extensive body of theoretical work[15-19] on these problems leads to a semiquantitative understanding of the magnetic and electronic properties[2,3,8-11] and a qualitative extension to periodic Kondo-like