

## van der Waals forces in electrorheological fluids

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It is well known that dipole-dipole forces (induced by external electric fields) between colloidal particles play a central role in determining the thermodynamic phases of electrorheological fluids. Here, it is argued that the long-range van der Waals forces induced by photon exchange also play an important role. A theory, which quantitatively includes the van der Waals interactions, is developed using statistical thermodynamic mean-field approximations. A comparison with an experimental phase separation is shown to be satisfactory.

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### I. INTRODUCTION

It is now widely recognized that many colloidal electrorheological (ER) fluids exhibit a phase separation into a colloidal "particle-rich phase" and a colloidal "particle-poor phase" when the external electric fields in the fluid are sufficiently strong [1–5]. If the colloidal particles are spherical and uniform in size, then it has been observed that the stable phase of the particle-rich phase is that of a bcc crystalline lattice forming "chains" parallel to the electric-field lines [1,6]. The mesoscopic picture is that the electric dipoles induced in the colloid particles by the external electric fields give rise to dipole-dipole interactions allowing the chains forming along the electric-field lines to lower the total free energy. However, the induced dipole-dipole interaction is not the only internal potential which must be taken into account when describing the thermodynamic properties of ER fluids. Also present in insulating colloidal fluids (even when external electric fields equal zero) are quantum electrodynamic fluctuations which give rise to long-range van der Waals forces. These have been studied extensively using the one-phonon loop contribution to the free energy [7–10], and have qualitatively been discussed for ER fluids [11].

Our purpose is to discuss the contribution to the thermodynamic properties of ER fluids made by quantum electrodynamic field fluctuations, i.e., the dispersion forces. In Sec. II, we modify a previously discussed mean-field theory of phase transitions in ER fluids [12] for the purpose of including the quantum electrodynamic van der Waals potentials into the free energy. In Sec. III, the resulting thermodynamic phase diagrams are shown. In Sec. IV, experimental determination of the van der Waals contribution are discussed, and the theoretical magnitude of the effect is estimated. Concluding remarks are made in Sec. V.

### II. THEORETICAL MODEL

We denote by  $x$  the "molecular" concentration of colloidal particles in the ER fluid, where each "molecule" of the colloidal particle is one mesoscopic solid particle, and each molecule of liquid is that number of liquid molecules

which would replace the volume of one colloidal solid particle. With this definition, the Gibbs free energy (per total number of molecules)  $\mu$  obeys the thermodynamic law [13]

$$d\mu = -sdT + vdP + \zeta dx - \mathbf{p} \cdot d\mathbf{E}, \quad (1)$$

where  $\mathbf{p}$  is the induced dipole moment (per total number of molecules); i.e., in terms of the dipole moment per unit volume  $\mathbf{P}$ ,

$$\mathbf{p} = v\mathbf{P}, \quad \mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}. \quad (2)$$

The mean-field treatment of the phase transition between a colloidal particle-poor (liquid) phase and a particle-rich (weak crystal) phase is then determined by an equation of state well known to describe phase separation in chemical mixtures; i.e.,

$$\zeta = \phi + kT \ln[x/(1-x)] - 2wx. \quad (3)$$

In the mean-field theory Eq. (3), both  $\phi$  and  $w$  can depend on temperature and electric field, however all the concentration  $x$  dependence has been made explicit. Within mean-field theory, the distinction between the dipole-dipole interactions and the quantum electrodynamic dispersion interactions can be described by the electric-field dependence of  $w$ . In detail

$$w = w_0 + \frac{1}{2}\alpha E^2, \quad (4)$$

where  $w_0$  is the strength of the interaction even when no mean macroscopic electric field is present, and  $\alpha$  is the effective net polarizability of the colloidal particle.

Equation (3) implies a phase separation for temperatures  $T < T_s$ , where

$$kT_s = (w_0 + \frac{1}{2}\alpha E^2) \{ (1-2x) / \ln[(1/x)-1] \}, \quad (5a)$$

or (equivalently) for electric fields  $E > E_s$ , where

$$E_s = \sqrt{(2kT[\ln(1/x)-1]) / \alpha(1-2x)} - (2w_0/\alpha). \quad (5b)$$

For sufficiently low temperature and/or high concentration, the phase separation will take place even when there is no external electric field.

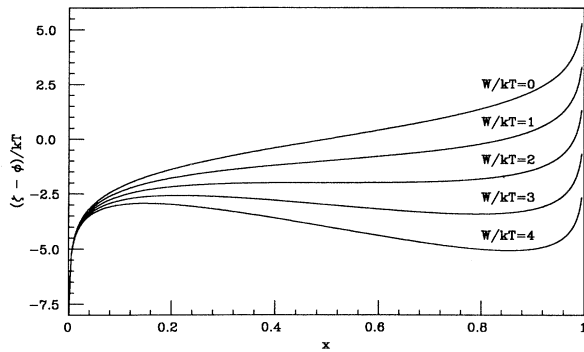


FIG. 1. Equation of state: relative chemical potential vs mole fraction for several values of the electronic interaction strength.

### III. PHASE DIAGRAMS

Let us now illustrate the phase diagrams for the theory. We show the equation of state, i.e., Eq. (3), in Fig. 1. Plotting  $\zeta$  versus  $x$  shows that for values of  $w/kT \geq 2$ ,  $\zeta$  is not single valued. An “equal-area” construction leads to Eq. (5a). The phase diagram in the  $(kT/w)$ - $x$  plane is shown in Fig. 2. Below the curve, determined by Eq. (5a), there exist two phases, and above the curve there is only one. Since one can cross this curve from above by lowering  $T$ , or by raising  $w$ , the phase transition can be induced by cooling, by increasing the dispersion interactions, or by applying an electric field. Figure 3 shows the electric field required for phase separation, as in Eq. (5b).  $E_s$  versus  $x$  is plotted for several values of  $w_0/kT$ . The shapes of the  $E_s$  versus  $x$  curves depend strongly on the value of  $(w_0/kT)$ .

### IV. COMPARISON TO EXPERIMENT

The experimental techniques for determining  $E_c$  have been previously described in detail elsewhere [14] and are based on defining a solid as a material that can support a shear, and a liquid as a material that cannot. The experimental phase diagram is shown in Fig. 4. The ER system that we measured consisted of 20- $\mu\text{m}$  spheres of aluminum (with a thin oxidized surface layer) suspended in

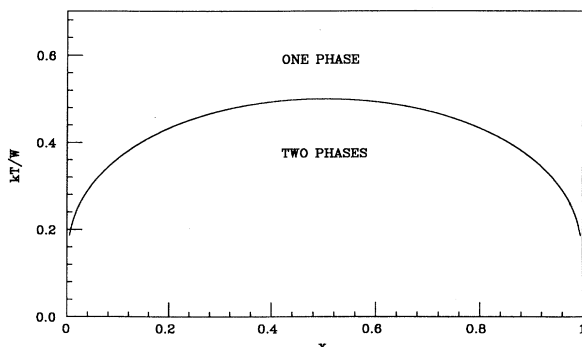


FIG. 2. Phase-separation diagram in the  $(kT/w)$ - $x$  plane.

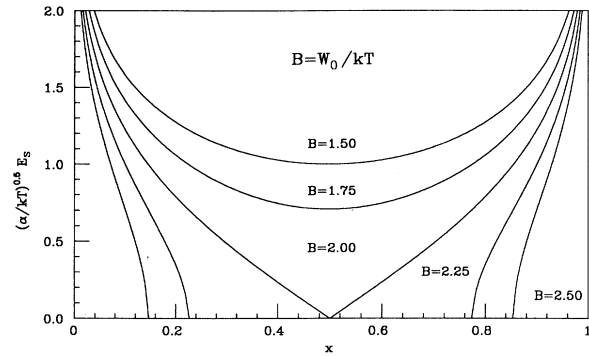


FIG. 3. Electric field required for phase separation vs mole fraction for several values of the van der Waals interaction strength.

mineral oil. The experiments were done at room temperature.

In view of aluminum being a conductor, we reasoned that the dipole-moment matrix elements for the two-photon exchange Van der Waals attraction would be large, and also more easily calculated in theory. Further, the induced dipole moments due to an external field would also be large allowing for the observed ER effects. Comparing the shape of the experimental curve in Fig. 4 to the theoretical curves in Fig. 3 confirms our expectations.

A  $\chi^2$  fit of the data to Eq. (5b) gives  $\alpha = 1.72 \times 10^{-14} \text{ cm}^3$  and  $w_0 = 8.84 \times 10^{-14} \text{ ergs}$ . This experiment demonstrates that for “good” ER systems, i.e., those in which the particulates have a much greater “effective dielectric constant” compared to the base fluid, the van der Waals effects cannot be ignored. We also fit, again, the data from work published earlier [12,14] on corn starch in mineral oil and found that van der Waals effects were also significant (although smaller) in this system where the particulate dielectric constant is closer in value to the base fluid’s [15]. A complete description of ER fluid-phase transitions should include these van der Waals attractions.

The value of  $w_0$ , determined experimentally, can be compared to the predicted value. For the case of “perfect metal spheres” of radius  $a$  (the polarizability of a per-

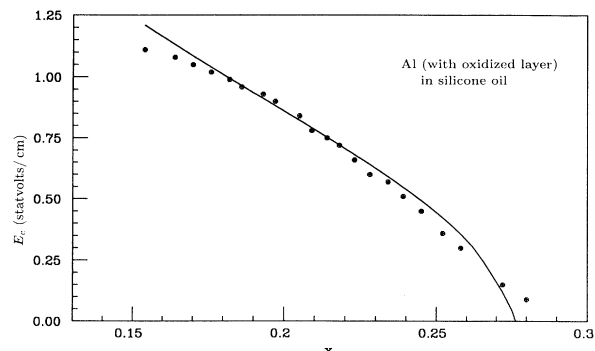


FIG. 4. Experimental phase diagram with a fit to theory.

fect metal sphere is equal to the radius cubed), in a fluid with dielectric response  $\epsilon$ , the value of the mean field  $w_0$  determined by two-photon exchange is given by [16]

$$w_0 = (3kTa^3/16\pi) \sum_{n=-\infty}^{\infty} (\omega_n/c)^4 \int_{r>a} d^3\mathbf{r} D_{ij}^2(\mathbf{r}, i|\omega_n|), \quad (6)$$

where  $\omega_n = (2\pi kT/\hbar)n$  and

$$D_{ij}(\mathbf{r}, z) = \int [d^3\mathbf{k}/(2\pi)^3] [4\pi e^{i\mathbf{k}\cdot\mathbf{r}} / (k^2 - (z/c)^2 \epsilon(z))] \times \{\delta_{ij} - [c^2 k_i k_j / z^2 \epsilon(z)]\} \quad (7)$$

is the photon propagator in the liquid. Using the known value of the dielectric constant of the fluid at zero frequency,  $\epsilon(z=0)$  and the known value of the particle ra-

dius  $a$ , numerical evaluation of Eq. (6) yields at room temperature

$$w_0 \sim 8 \times 10^{-14} \text{ erg},$$

remarkably close to the experimental value.

## V. CONCLUSION

The central point of this work concerning the importance of dispersion forces in ER fluids is the following. The dispersion forces alone lead to the clustering of groups of colloidal particles; the external electric field completes the job of phase separation into the weak crystalline state. Therefore, a complete theory of electrorheology must quantitatively include these effects.

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