Percolation in interacting colloids

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The percolation behavior of spherical particles with attractive interactions is studied with use of Monte Carlo simulations. These systems differ from lattice Ising systems, which have been previously analyzed, in the necessity to define a shell parameter δ to specify a connected cluster. For small values of δ, correlations due to the attractive interactions drastically lower the percolation threshold in the vicinity of the gas-liquid critical point. For larger values of δ, these shifts are smaller, but the effects of long-range correlations show up as enhanced finite-size effects. The simulation results are discussed in the light of recent experiments which measure the temperature and concentration dependence of the conductivity in interacting microemulsions.

I. INTRODUCTION

The concept of a percolation transition is often used in interpreting the conductivity of disordered systems.[1] In systems with completely random distributions of particles, the percolation transition signifies the existence of an infinite cluster which becomes more and more probable as the volume fraction ϕ approaches its critical value ϕ_p. In systems of interacting particles, it is not merely the increase in concentration that determines whether the system percolates. Interactions between the particles induce positional correlations which can give rise to an infinite cluster even when the concentration of particles is relatively small.[2–6]

Recent measurements of the conductivity of microemulsions (spherical dispersions of water in oil with surfactant at the globule interface) have suggested the existence of a percolation threshold as a function of both volume fraction[7–9] and temperature.[9] The microemulsion systems differ from the hard-sphere mixtures in two important respects: (1) The surfactant-coated globules of water in oil (radius ~ 75 Å) are much bigger than the oil molecules. The problem is not one of a mixture of conducting and nonconducting spheres, but rather of percolation of the globules in the continuum oil background. (At low to moderate $\sim 20\%$ volume fractions, the globules are spherical and quite monodispersed in some recently studied systems.[10]) (2) Recent experimental[10,11] and theoretical[12] studies have shown that attractive interactions between the globules are crucial in understanding the phase diagram and scattering data.

The experimental studies of these microemulsion systems[7–9] show percolation behavior at small ($\sim 7\%$) volume fractions—much smaller than predicted by lattice[13] theories. In addition, recent experiments[9] have shown a sharp rise in the conductivity as the temperature is changed and the system approaches a liquid-gas phase transition.[12,14]

Motivated by these results we have analyzed the percolation behavior of spherical particles with short-ranged attractions using Monte Carlo (MC) simulations. Previous studies of attractive systems have focused on lattice (spin) models;[2–4] continuum models have only been studied in the hard-particle limit.[5] Some analysis of the problem of attracting spheres has been performed using cluster expansions;[6] however, the approximations involved preclude quantitative agreement with known simulation results even in the noninteracting limit.

The main difference between the continuum and lattice studies of interacting systems lies in ambiguity in the definition of a connected cluster in the continuum case. There are several ways to define off-lattice percolation problems. (a) Percolation in a binary mixture of closely packed spheres, where $\phi_p \cong 0.16$–0.18 in $d=3$.[1,13(a)] The close packing provides a quasilattice for the conducting spheres and it is not surprising that the lattice results normalized by the close-packing volume fraction are applicable.[13(a)] (b) Percolation of a set of points where connectedness of two points is determined by the existence of a common face of the corresponding Voronoi polyhedra. Here $\phi_p \cong 0.15$.[13(a)–13(c)] (c) Percolation of a random set of points, where two points are considered connected if the distance between them is smaller than some radius r_0. Here $\phi_p \cong 0.35$ for $d=3$, where $\phi = 4\pi r_0^3 n/3$ and n is the density of points.[13(d)] (d) Percolation of hard spheres in a continuum background where it is required that the spheres touch in order to conduct. Percolation is expected to occur near the close-packing volume fraction of 0.65.

Since none of these models is suitable for the colloidal problem, we define percolation in the system of interacting spheres as follows: The configurations of the system belong to an equilibrium ensemble at temperature T and volume fraction $\phi = 4\pi R^3 n/3$, where $n = N/V$ is the number density of spheres, N is the number of particles, V is the total volume, and R is the hard-core radius. To define connectedness we introduce the parameter δ, where $\delta/2$ is the width of a shell around each hard core. If two shells overlap, the corresponding spheres are considered to be connected and hence in the same cluster. This parameter is not needed for the definition of interacting percolation on a lattice since two occupied nearest-neighbor sites are always in the same cluster. We study the percolation properties of the system of spherical particles as a function of temperature (or interaction strength), volume frac-

tion, and shell size. Depending on the ratio of the shell size to the hard-core radius, the change in ϕ_p varies from a factor of 4 down to changes of only 30%. For very small shell sizes relative to the globule size, the effects of the interparticle attractions are large. At infinite temperature, the system percolates only at very high volume fractions, close to the random-close-packing density ($\sim 65\%$). As the temperature is lowered[15] and the phase separation is approached, ϕ_p is drastically reduced. The magnitude of this reduction depends on the shell size. For small shells ϕ_p is reduced from $\sim 65\%$ to $\sim 10\%$. For larger shells, we find that the percolation threshold is only slightly modified by the attractive interactions as the critical point for phase separation is approached, although the value of ϕ_p can be quite low. The modification in ϕ_p is of the order of (30—40%) in the direction of lowering ϕ_p and is qualitatively the same as the results of the lattice calculations[4] (e.g., for a cubic lattice, ϕ_p shifts from 31% to 22% as temperature T is lowered from infinity to $0.96T_c$).

Our results show that the discussion of a "universal" percolation threshold of 15% for hard spheres[7,8] and used in the analysis of microemulsion conductivity is not meaningful. The observed experimental values for the ϕ_p depend on the "shell" through which conduction occurs as well as on the magnitude of the attractive interactions. The size of the shell can be estimated from our simulations as discussed in Sec. IV, while the range and magnitude of the attractive interactions can be determined from thermodynamic or scattering measurements (see Ref. 10).

The organization of this paper is as follows. In Sec. II we discuss the model and the method used in our MC simulation. The results of these simulations are presented in Sec. III which shows the change in the percolation threshold as a function of volume fraction, temperature, and shell size. A summary and discussion follow in Sec. IV.

II. MODEL AND SIMULATION

The MC simulations model a system of spherical particles with a hard-core diameter, which we take to be 1. The attractive interaction is modeled as a square well of width λ (relative to the hard-core diameter), so that the interaction potential $V(\mathbf{r})$ is given by

$$V(r)=\begin{cases}\infty & \text{for } r<1,\\ -\epsilon kT & \text{for } 1\le r\le 1+\lambda,\end{cases} \tag{1}$$

where $\mathbf{r}$ is the interparticle separation. Standard Metropolis[10,16] algorithms were used for systems of 108, 500, and 2048 particles in a cubic box with periodic boundary conditions. A table of interacting neighbors was constructed every 10 MC steps to facilitate the calculation. For small values of λ and for temperatures near the critical point, 20 000 MC steps per particle were used to equilibrate the system and an additional 20 000 MC steps per particle were run for the cluster calculations. Typical runs for larger values of $\lambda \sim 0.1$ used 4000—10 000 MC steps per particle.

The model with short-range attractions is motivated by recent results[10] on microemulsions which show that the neutron-scattering structure factor can be fit with a model of square-well attractions with a short range (3 Å) compared to the globule diameter (typically ~ 60 Å). The physical origin of this extremely short-ranged interaction is the overlapping of the surfactant tails which protrude from the globules. The interaction range is limited due to steric effects.[10,11] In Ref. 10 it was shown that the interaction strength ϵ increases linearly with the globule radius and is sufficient to cause the liquid-gas phase separation observed in these systems. A mean-field calculation[12] (which keeps high-order terms in the hard-core interactions) shows that the critical volume fraction for phase separation $\phi_c \cong 0.13$, while the critical value of ϵ, defined by ϵ_c, is determined by

$$[(1+\lambda)^3-1](e^{\epsilon}-1)\cong \tfrac{21}{8}\ . \tag{2}$$

The mean-field results are probably an underestimate of ϵ_c due to fluctuations which destabilize the system.

It is difficult to locate the coexistence curve accurately with the small systems used in our simulations. To check the mean-field prediction of $\phi_c = 0.13$, we computed the rms potential-energy fluctuations as a function of ϕ. Figure 1 shows the relative potential-energy fluctuations as a function of volume fraction for $\lambda = 0.1$, $\epsilon = 2$ ($\epsilon_c = 2.4$ in mean field) for a 500 particle simulation of 10 000 MC steps per particle. The largest relative fluctuations are seen to occur in the region of 13% indicating the approximate applicability of the mean-field result. In Fig. 2 we present an analysis of the density fluctuations in our system as a function of volume fraction for $\lambda = 0.1$ and $\epsilon = 2.1$. The density fluctuations are studied by dividing the cubic system into either 8 or 27 smaller cubes.[17] Histograms of the population of each of the smaller cubes were obtained throughout the runs; a single peak in these histograms indicates a one-phase system, while a multiple-peaked structure indicates a phase separated one. The runs with volume fractions of 14% showed large

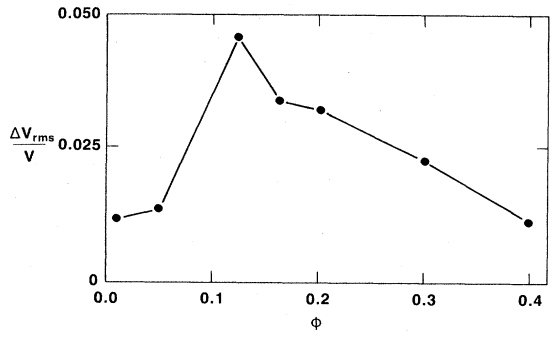

FIG. 1. Relative potential-energy fluctuation; V is the average potential energy per particle and ΔV is the rms fluctuation. The relative energy fluctuation is plotted as a function of the volume fraction ϕ for a square-well interaction with range $\lambda = 0.1$ and for a depth $\epsilon = 2$. The simulations were performed on a system of 500 particles and data were averaged over 10 000 MC steps per particle.

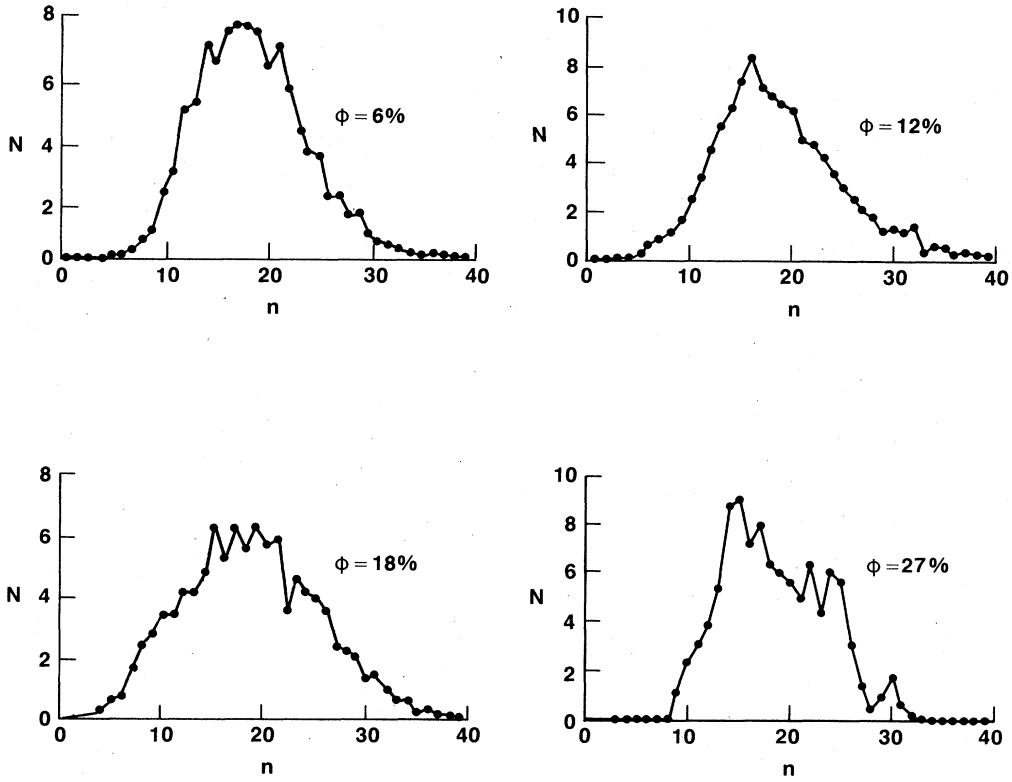

FIG. 2. Histograms of the average number of particles in each of 27 boxes for a 500-particle system for $\lambda=0.1$ and $\epsilon=2.1$. The histograms are shown for volume fractions ranging from 6% to 27% and are indicative of the density fluctuations in the system.

variations in the rms fluctuations, indicating that ϕ_c is in this neighborhood. These results are in agreement with an early calculation of Baxter[18] using Percus-Yevick theory and the compressibility equation of state. The existence of ϕ_c in the vicinity of $\phi=0.15$ is in disagreement with a later calculation of the coexistence curve by Watts *et al.*[19] using the energy equation of state; their estimate of $\phi_c \cong 30\%$ is outside the range of error of our simulations.

The MC simulations yield the positions of all the interacting particles at every time step. To study the percolation transition which occurs when an infinite (system size) cluster is first formed, one must first have a precise definition of the cluster. For lattice problems, two nearest neighbors are always in contact so that the cluster definition is straightforward. In a continuum, one must specify the interparticle spacing at which two globules are considered to be in the same cluster. In our simulations, we have specified a shell parameter δ which is the size of a spherical shell around the hard-core diameter. Two particles are considered to be in a cluster when their centers are separated by a distance less than $1+\delta$ (δ is in units of the particle diameter). The physical origin of this shell must be considered in light of the conductivity mechanism for each specific case. In the present work, we take δ as a parameter and study its role in the percolation threshold.

The actual percolation calculation is performed every 50—100 MC steps per particle. The percolation behavior is examined by a search for a cluster of particles which connects any pair of opposite faces of the box. The percolation probability P is the fraction of configurations tested where such a cluster has been found. We compute P as a function of well depth ϵ, volume fraction ϕ, and shell size δ. Note that in the limit of an infinite system, the percolation probability should be 1 above ϕ_p and 0 below. The deviation from this behavior, evident in our simulations (see Figs. 3—8 below), reflects the fluctuations due to the finite size of our system. The percolation threshold is determined from the value of ϕ where $P=\frac{1}{2}$ or from the maximum slope of P versus ϕ.

III. PERCOLATION THRESHOLD

In this section we present the results of the MC simulations and of the percolation analysis. The percolation probability is shown as a function of the shell δ, well depth ϵ, and volume fraction.

For small values of ϵ, where interactions can be neglected, the percolation probability is a function of both δ and the volume fraction ϕ. This is shown in Fig. 3, where the percolation probability P is plotted as a function of δ for values of $0.05 \leq \phi \leq 0.20$. As expected, the percolation threshold (defined by the point of maximum slope) decreases as ϕ is increased. A comparison of these plots and actual experimental data in a region far from the critical point will yield an appropriate value of δ.

A more compact representation of the data for the noninteracting system is shown in Fig. 4 where P is plot-

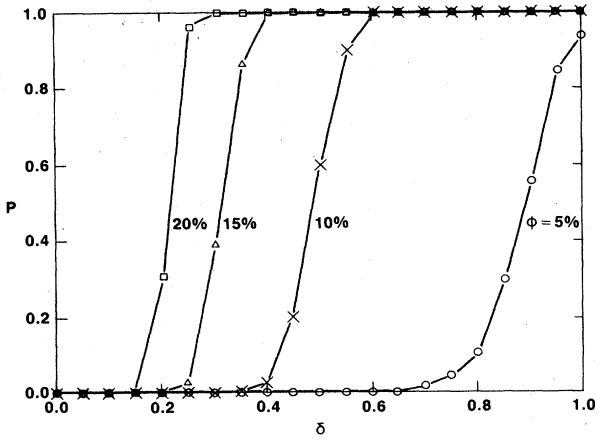

FIG. 3. Percolation probability P as a function of the shell δ for various values of the volume fraction. These results are for a 500-particle system with no attractive interactions ($\epsilon=0$).

ted as a function of the scaled variable $\bar{\phi}=\phi(1+\delta)^3$. The parameter $\bar{\phi}$ is proportional to the effective volume fraction including the shell. For small values of the hard-core volume fraction ϕ, the curves for different ϕ all scale and show a percolation threshold $\bar{\phi}_p \cong 0.35$. This effect is even seen in the 108 particle system, but is of course sharpest for the 2048 particle simulation. This value for $\bar{\phi}_p$ is in agreement with the results for continuum percolation where overlap is allowed;[20] for small values of ϕ, most of the effective volume is occupied by the shell so that the hard-core effects are negligible. We have also verified that for small values of the shell ($\delta \cong 0.01$), the percolation threshold in the noninteracting limit is close to the random-close-packing density $\phi \cong 0.65$. Although equilibration is difficult at such high densities, we have seen no percolation in samples of $\phi \leq 0.50$ with $\delta=0.01$.

As the interactions are increased, the percolation threshold is lowered. This is shown in Figs. 5 and 6

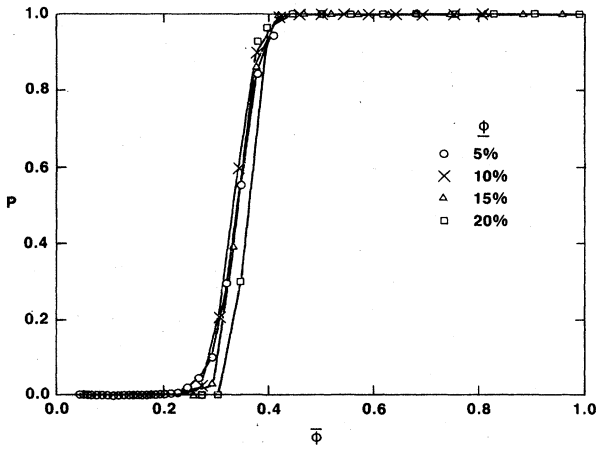

FIG. 4. Percolation probability P as a function of the scaled volume fraction for the system described in Fig. 3. The scaled volume fraction $\bar{\phi}=\phi(1+\delta)^3$. Note that the scaling breaks down as the hard-core volume fraction increases and the limit of overlapping spheres becomes less relevant.

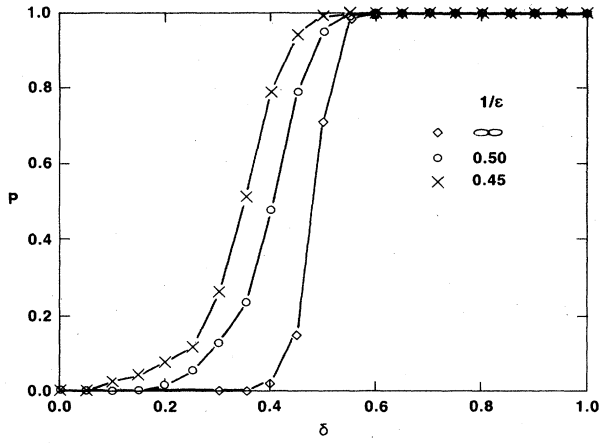

FIG. 5. Percolation probability P plotted as a function of the shell parameter δ for various values of ϵ. The simulations were performed on 2048 particles and averaged over 4000 MC steps per particle. The attraction range $\lambda=0.1$ and the volume fraction $\phi=0.1$.

where P is plotted as a function of δ and ϕ, respectively, for $\lambda=0.1$. The simulations were run on 500-particle systems for various values of ϵ up to $\epsilon \cong \epsilon_c$. For relatively large values of δ (e.g., $\delta \sim 0.5$), the decrease in the percolation threshold ϕ_p is of the order of (30—50)%, similar to the results in lattice systems.[2–4] We note that in contrast to the curves for P for small ϵ, the plots of P versus δ and ϕ are not nearly as sharp. This indicates the increased sensitivity to finite-size effects due to critical-type fluctuations; the unit of length is now the correlation length and not the globule size. Our system (with a fixed number of particles, e.g., 500) is now effectively smaller and finite-size smearing of ϕ_p is more pronounced.

In contrast to the relatively small changes in ϕ_p observed for large values of δ, the effects for small values of δ (e.g., $\delta \sim 0.01$) are more pronounced; ϕ_p is decreased from the neighborhood of the random-close-packing density, to values near the critical density. This is shown in Fig. 7 where P is plotted as a function of ϕ for values of $\delta=0.01$, $\lambda=0.01$ and interaction strengths $\epsilon=4.2$ and 3.3

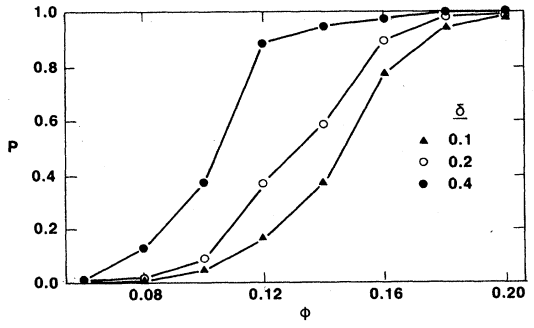

FIG. 6. Percolation probability P as a function of volume fraction ϕ for $\lambda=0.1$ and $\epsilon=2.1$. P is shown for various values of the shell parameter δ. The simulations were run on 500-particle systems and averaged over 60 000 MC steps per particle.

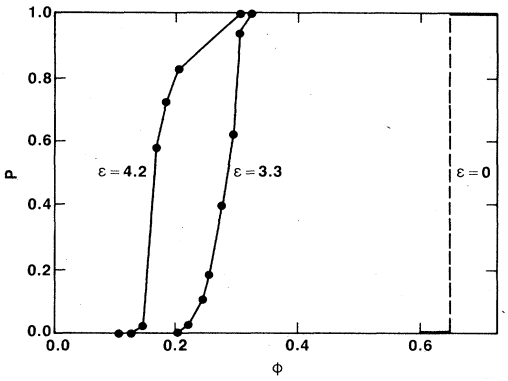

FIG. 7. Percolation probability P as a function of the volume fraction ϕ for a very short-range interaction $\lambda=0.01$ and a shell parameter $\delta=0.01$. The values of ϵ are 4.17 and 3.33 (the critical value of ϵ is 4.46 in mean-field theory). For $\epsilon\cong 0$, the system did not show any percolation for $\phi\leq 0.50$ and the random-close-packed value of $\phi=0.65$ is shown.

(the mean-field value of $\epsilon_c=4.47$). Since we lose sensitivity to the interactions when $\delta<\lambda$, we must reduce λ to study the effects of small δ. We note that ϕ_p has shifted from $\sim 65\%$ to $\sim 14\%$. The largest jump in P is in this neighborhood with a much more gradual increase as ϕ is further increased, signifying the role of ϕ_c for phase separation. The increased correlation length in the neighborhood of the critical point renormalizes the percolation problem to a percolation of correlated regions or blobs mean size $\xi(\epsilon,\phi)$. These regions are both anisotropic[20,21] and fractal and one would expect their percolation threshold to be lower than that of compact spheres. The percolation threshold ϕ_p is then determined by the condition that $n_b\xi^d(\epsilon,\phi)=c$ where n_b is the number density of blobs and c is a constant of order unity.

Taking into account the fractal dimensionality of these regions near the critical point where the fractal dimension $D=d-\beta/\nu$, we find the self-consistent relation for ϕ_p,

$$\phi_p=c[\xi(\epsilon,\phi_p)]^{-\beta/\nu}.$$

Another mechanism which tends to lower the percolation threshold is the anisotropy of the correlated regions. The critical volume fraction for percolation of elongated objects[20] is lower than that of spherical ones. This mechanism is probably responsible for the initial decrease of ϕ_p when ϵ is still far from ϵ_c. It is interesting that in Fig. 6 we see that even for $\lambda=0.1$, for small $\delta=0.1$, the percolation threshold is reduced to near ϕ_c as well; the critical volume fraction may represent a lower limit to ϕ_p for small values of δ.

IV. SUMMARY

We have studied the percolation behavior of colloidal particles with attractive interactions. In contrast to the lattice systems, an additional parameter, the shell size δ, is necessary to define percolation in these continuum systems. Using Monte Carlo simulations we have calculated the percolation probability as a function of shell size, volume fraction, and well depth for spherical particles interacting with a square-well potential. For $\epsilon=0$ (i.e., only hard-core repulsions), we find that we can define an effective volume fraction $\bar{\phi}=\phi(1+\delta)^3$. For small values of ϕ, the percolation threshold is given by $\bar{\phi}\cong 0.35$, consistent with known results for continuum percolation.

These results demonstrate the ambiguity of the value of ϕ_p in continuum systems. The commonly referred to[7,8] value of 15% for hard-sphere percolation used in the analysis of microemulsion data is irrelevant. The observed threshold is due to (i) a shell of $\delta\cong 0.4$ if the attractive interactions are neglected and/or (ii) clustering due to attractions. In either case, the value of $\phi_p\cong 0.15$ should vary as the surfactant properties are changed (and the shell size increased or decreased) or as the size of the globule or temperature (which determine the strength of the attractions[10]) is changed.

At finite values of $\epsilon<\epsilon_c$ for phase separation, we find that the percolation threshold shifts to smaller values of ϕ for a given δ or to smaller values of δ for a given value of ϕ. We associate this with the formation of correlated clusters in the interacting system. These clusters are both anisotropic and fractal-like, and their percolation thresholds should be lower than that of spheres.[21] For small values of δ and λ, the effects of these correlations are large; ϕ is reduced from ϕ for random close packing (at $\epsilon=0$) to ϕ on the order of ϕ_c ($\approx 13\%$) for phase separation. It is at ϕ_c that the correlations in the system are the strongest and the percolation threshold is reduced to near this value. The results are summarized in Fig. 8 where we schematically show the reduction of the percolation threshold as a function of temperature for short-ranged interactions ($\lambda\ll 1$). For $1>\delta>\lambda$, the system percolates at a relatively small value of ϕ even for $\epsilon=0$, so that increasing ϵ has only a nominal effect on reducing ϕ_p, although the value of ϕ_p can be arbitrarily small for large

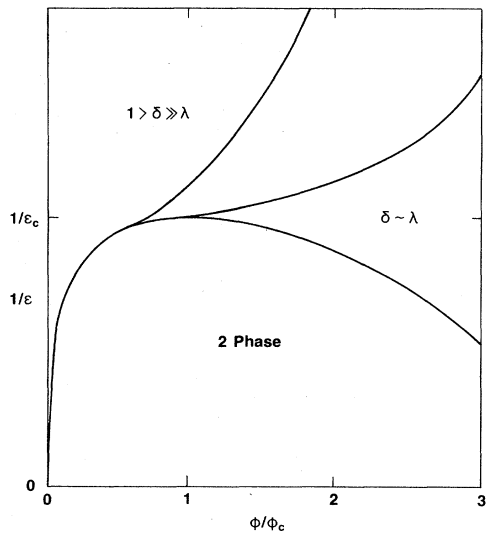

FIG. 8. Schematic plot of the change in the percolation threshold as a function of ϵ for short-ranged interactions, $\lambda\ll 1$ for values of the shell δ both much larger and comparable to λ. The coexistence curve is derived from a mean-field theory (Ref. 12). The well depth is ϵ and the volume fraction is ϕ.

δ. On the other hand, for $\delta=\lambda \ll 1$, the effect of increasing ϵ is much larger as discussed above. These simulations suggest that the critical volume for phase separation may be a lower limit for the percolation threshold for systems with very thin shells, δ small.

The applicability of these results to experimental systems depends on the physics of the conduction mechanism and the existence of a static shell parameter δ. Far away from the critical point, the value of δ can be determined by comparing the percolation threshold with Fig. 4. Assuming constant δ, the reduction of the percolation threshold near the critical point can be predicted from Fig. 6 and compared with experiment. Our theoretical results qualitatively explain the observed[9] reduction of ϕ_p as the temperature approaches the critical temperature for phase-separation (see Ref. 15 for an important note) transition.

Previous scaling arguments[7] have indicated that while the critical exponents for "stirred percolation"[7] (i.e., percolation in a diffusing system) are modified, the percolation threshold retains its static value. In the present simulations, the dynamics was taken into account only in terms of an ensemble average being performed by a time average of the system as it evolved in equilibrium. Future reports[22] will present simulation results which properly calculate the exponents and thresholds for the stirred case.

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