Do Interactions Raise or Lower a Percolation Threshold?

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A Monte Carlo study of spherical particles shows that increased interaction strength may either raise or lower the volume fraction required for percolation. The sense of the change depends on the distance at which two particles are considered connected, the dimensionality, and the proximity to the critical temperature. An on-lattice simulation supports the continuum result.

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Though early studies of percolation theory described simple random systems on a lattice, recent studies have treated diverse models which may be off lattice,[1,2] have correlated occupancy,[3] and/or involve particles which interact at thermal equilibrium.[4–6] Microemulsions, for example, are tricomponent systems of oil, water, and surfactant with these properties; globules exhibit a percolation threshold for ionic conductivity which depends strongly on interaction strength.[7] Previous investigations have concluded that attractive interactions (or positive correlations) between particles lower the percolation threshold, ϕ_p.[3–6] We find, however, that in general, clustering due to interparticle attraction may raise or lower ϕ_p.

Our computer model[8] is an off-lattice system of particles undergoing Brownian motion via a Monte Carlo algorithm. These colloidal particles have both an excluded-volume repulsion and a short-ranged attraction: $U(r)=\infty$ for $r<a$, $-\epsilon$ for $a\leqslant r<a(1+\lambda)$ and 0 for $a(1+\lambda)\leqslant r$. The hard-core diameter is a; the interaction range λ is fixed at 0.1 for this study. 400 particles [two dimensions (2D)] or 500 particles (3D) are allowed to reach thermal equilibrium ($\sim 40\,000$ steps per particle), and then the instantaneous configuration of the particles is tested every few hundred steps for the existence of a spanning cluster. One constructs a shell of diameter $a(1+\delta)$ about each particle's center and asserts that two particles are connected if their shells overlap. Some generalized criterion, such as this one, for the connectedness of two particles is necessary in the continuum.[1] The distance $a\delta$ may be thought of as the range across which an excitation may "hop" from one particle to another.

The results of these simulations are obtained at fixed a for various particle densities, ρ. All runs are performed in the one-phase region. At each value of $\phi=\pi\rho a^2/4$ (2D), or $\phi=\pi\rho a^3/6$ (3D), the periodic searches generate the probability that a spanning cluster exists as a function of δ. Such curves are found in Ref. 8; we take the value of δ at which this probability is 0.5 as δ_p, the value at threshold.

Our continuum results are summarized for $d=2$ in Fig. 1(a), which is a phase diagram for fixed δ_p. The curves dividing percolating from nonpercolating regimes are parametrized by ϵ. The coexistence curve is approximate. By definition, different curves parametrized by δ_p cannot cross one another, and all curves with $\delta_p>\lambda$ must meet the coexistence curve at or to the left-hand side of the critical point.[4a] For an intermediate value of δ_p, the percolation line bends toward higher ϕ for ϵ small but, constrained to meet the coexistence curve to the left of ϕ_c, bends in the opposite direction for larger ϵ near ϵ_c.

Our novel result, that an increase in ϵ may increase ϕ_p, is not an artifact of the continuum nature of the simulation. If one retains the freedom of assigning the range at which particles are connected, the new behavior is also seen on a lattice. Figure 1(b) is the result of a conventional 2D lattice-gas simulation on a square lattice with nearest-neighbor interactions.[9] In this simulation, two occupied sites were considered connected if they were separated by a geometrical distance less than or equal to some value R, the lattice analog of δ.[10] For nearest-neighbor connectedness ($R=1$), we find only the conventional results, which agree with the data of Vicsek.[11] As a consequence of the fact that two phases may not percolate simultaneously in two dimensions, this percolation line must meet the coexistence curve at the critical point,[4a] which is $\phi_c=\frac{1}{2}$ for a lattice gas. However, for $R>1$, no such topological restriction exists; the "shell" about each occupied site is permeable. Thus, curves for $R>1$ are free to meet the coexistence curve at $\phi<\phi_c$. In Fig. 1(b) one sees bending of the percolation line toward higher volume fractions with R only as large as 2 (with next-nearest-neighbor connectedness).

We will now argue that our novel result arises from the generality of δ, i.e., from the independence of δ and λ which allows the hopping range to exceed the in-

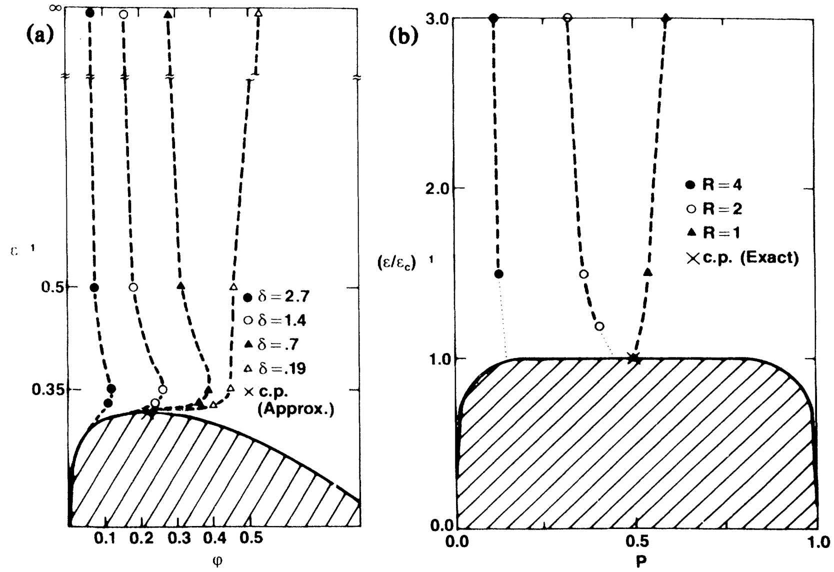

FIG. 1. Dashed lines divide percolating (right-hand side of line) from nonpercolating regions for the given δ_p in 2D. (a) Continuum simulation. (b) Lattice-gas simulation. R is the range (Ref. 9) over which occupied sites are considered connected. The fine dotted lines are a guide to the eye.

teraction range. As a first step in the argument, consider the simplest case, that of $\lambda = 0$. Particles do not attract one another and each consists of an impermeable core surrounded by a completely permeable outer shell. When the shells of adjacent particles overlap, they are said to be connected. If we imagine varying the ratio of the shell radius to the core radius, two geometrical effects make competing predictions: (i) For a system to percolate, pairs of particles must have shells which overlap. Thus, particles with a greater ratio of shell to core have a greater probability for pairwise overlap; their threshold is lowered. (ii) At threshold, the correlation length for connectedness, ξ_p, diverges and a spanning cluster appears. Particles with a greater ratio of shell to core have a smaller mean radius for clusters of a given mass, and hence their percolation threshold is raised.

Now we extend the argument to the full case, where $\lambda, \epsilon \neq 0$. The competing trends predicted by (i) and (ii) still exist because of the following analogy between the $\epsilon = 0$ and $\epsilon \neq 0$ cases: Far from the critical point, an increase in attraction strength (ϵ) is analogous to a decrease in the ratio of shell to core (if the range of attraction is less than the permeable-shell radius). That is, an increase in ϵ will (i) promote pairwise overlap, but (ii) render clusters more compact. Thus, ϕ_p may rise or fall with interaction strength. Figure 2 illustrates the compaction of clusters which leads to an increase in threshold. Previous work on lattice did not reveal both trends because only nearest neighbors were connected; the shell radius was fixed at the interaction range. Previous work off lattice investigated the case of a vanishingly small shell,[6] or looked in detail only at the lowest-order term in a series expansion for the threshold.[5] These found only the trend given by argument (i) above.

To view the effects of interaction on clustering and clustering on threshold, an alternative way of viewing the data from that of Fig. 1 is needed. For example, one wishes to know the hopping range, δ_p, which just allows a sample of a given ϕ, ϵ to percolate. So consider Fig. 3, which plots, as a function of ϕ, $\bar{\phi}_p$, the reduced volume fraction of Ref. 8. $\bar{\phi}_p$ has the appeal of an "effective" volume fraction; it is defined as $\bar{\phi}_p = \phi(1+\delta_p)^d$ and it is simply the volume fraction of the hard core plus shell at percolation threshold. From Fig. 3, in the absence of attractive interactions, $\bar{\phi}_p$ vs ϕ displays a minimum in both 2D and 3D. Further, the effect of attraction is to increase $\bar{\phi}_p$ for low ϕ, and

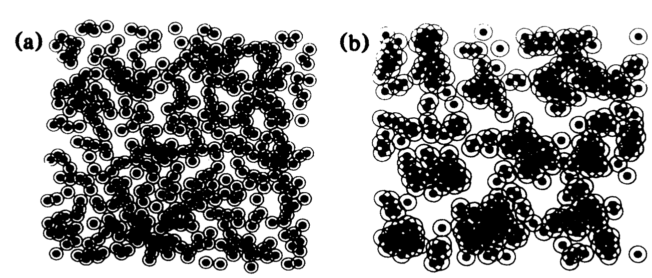

FIG. 2. Hard particles with permeable shells in 2D; $\phi = 0.24$. The radius of the shell is chosen so that system is at its percolation threshold. (a) No attraction. (b) Attraction leading to clustering.

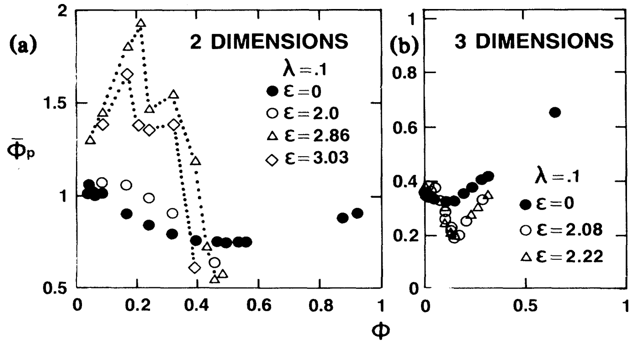

FIG. 3. Reduced volume fraction (Ref. 8) at percolation threshold as a function of volume fraction. Filled circles at $\phi \cong 0.91$ (2D) and $\phi \cong 0.64$ (3D) are exact values for random close packing. For ϵ large, local minima are centered at ϕ_c in 2D and 3D. (a) In 2D for small ϕ, $\bar{\phi}_p$ rises and then falls with ϵ. Dotted lines are a guide to the eye. (b) In 3D, attractions raise $\bar{\phi}_p$ for small ϕ, and lower it for larger ϕ.

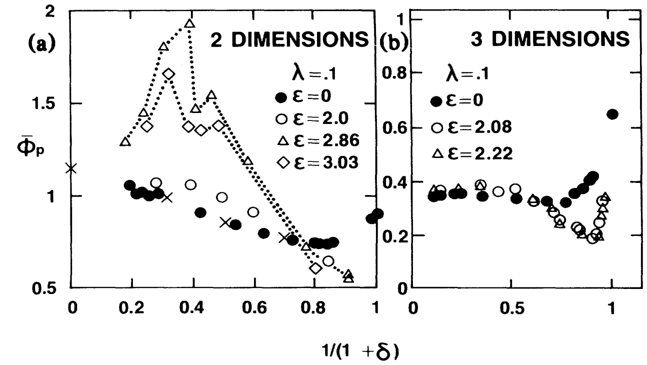

FIG. 4. Reduced volume fraction at threshold as a function of hard-core fraction. Crosses are derived from Table II of Ref. 1.

decrease it for high ϕ. Finally, local minima appear at the estimated critical density for phase separation in 2D and 3D near the critical temperature. The approximate critical volume fractions are [12] $\phi_c \cong 0.22$ (2D) and $\cong 0.13$ (3D), consistent with the extrema in Fig. 3.

To apply arguments (i) and (ii), it is useful to transform the horizontal axis of Fig. 3 as in Fig. 4. There, the independent variable is the hard-core radius fraction, $1/(1+\delta)$.[13] Zero hard-core fraction represents completely permeable particles; a hard-core fraction of unity represents impenetrable objects. Again, consider first the simplest case, $\epsilon, \lambda = 0$. It is now straightforward to evaluate the outcome of the competition between effects (i) and (ii) from the filled circles of Fig. 4. In 2D and 3D, for $\epsilon = 0$, effect (ii) dominates for small hard-core fractions, and effect (i) for large ones. The decrease in $\bar{\phi}_p$ with $1/(1+\delta)$ (to the left-hand side of the minimum) in Fig. 4(a) agrees quantitatively with Ref. 1, and agrees with the trend seen by Gawlinski and Redner[14] for oriented square elements.

A rigorous way to evaluate the outcome of the competition between (i) and (ii) is to employ an exact series developed by Coniglio and co-workers[5]: To lowest order in ϕ_p for the case $\epsilon = 0$,

$$\bar{\phi}_p \cong \{2^d[1 - 1/(1+\delta)^d]\}^{-1}.$$

This term predicts the behavior (i); $\bar{\phi}_p$ is inversely proportional to the phase space for pairwise overlap. At next order in ϕ_p, the series for $S(\phi)$, the mean cluster size, produces an estimate of $\bar{\phi}_p$ from the ratio test. For a nonvanishing but small, the new term predicts $d\bar{\phi}_p/da\,|_{a(1+\delta)=1} \cong -b_n a^{n-1}$ in n dimensions with $b_2 = 1.209$, $b_3 = \frac{12}{17}$. Thus for a small [equivalently, $1/(1+\delta)$ small] an increase in the hard-core fraction decreases the percolation threshold $\bar{\phi}_p$; the decrease is linear in $1/(1+\delta)$ only in 2D and is progressively weaker in higher dimension. This predicted dominance of effect (ii) for small $1+\delta$ is seen in Fig. 4. It has been shown that in infinite dimension, all virial coefficients vanish in units of the second[15]; a consequence is that for $d = \infty$, there is no second-term correction to the expression for $\bar{\phi}_p$ above. Thus for a/δ small, effect (ii) is absent in infinite dimension.

Now consider the case $\epsilon, \lambda \neq 0$; how should we expect the attractive interactions to affect the percolation threshold? To first order in ϕ_p,

$$\bar{\phi}_p \cong \left\{2^d\left[(e^\epsilon - 1)\frac{(1+\lambda)^d}{(1+\delta)^d} + 1 - \frac{e^\epsilon}{(1+\delta)^d}\right]\right\}^{-1},$$

where $\lambda \leq \delta$. One can pursue the series to higher order, based on known virial integrals,[16] but even the next term is quite complicated. However, alteration of ϵ should effect the threshold as would alternation of $1/(1+\delta)$ in the opposite direction. This is apparent in the lowest-order approximation to $\bar{\phi}_p$ above. Indeed, in Figs. 4(a) and 4(b), in the region where an increase of $1/(1+\delta)$ with $\epsilon = 0$ lowers $\bar{\phi}_p$, an increase of ϵ for fixed $1/(1+\delta)$ raises $\bar{\phi}_p$. For larger $1/(1+\delta)$, where an increase of $1/(1+\delta)$ raises $\bar{\phi}_p$, an increase of ϵ lowers $\bar{\phi}_p$.

This simple line of reasoning must be suspended near the coexistence curve. For $d = 2$, the critical density lies in a region where decreased clustering aids percolation; for ϵ not too large, a maximum appears in $\bar{\phi}_p$. However, as ϵ_c is approached, $\bar{\phi}_p$ reverses its trend of increase and a minimum forms about the critical density. This must occur as a consequence of the Fisher droplet picture of the critical point.[17] It has been rigorously shown that for a lattice gas,[4a] $\xi_p \geq \xi_T$; i.e., the correlation length for nearest-neighbor connectivity exceeds the thermal correlation length. For our off-lattice system, the correct generalization is that for $\delta \sim \lambda$, $\xi_p \geqslant \xi_T$. That is, there must be a nonvanishing probability that particles are connected with δ not greater than the interaction range in order for them to display nonvanishing density fluctuations about the mean density. Thus, near ϵ_c, Figs. 3(a) and 3(b) show minima centered at ϕ_c. And in Fig. 1(a) for δ near λ, ϕ_p decreases sharply with increasing ϵ in the neighborhood of the critical point.

In conclusion, interactions may raise or lower a percolation threshold on or off a lattice, given a general definition of connectedness. We gratefully acknowledge conversations with S. Alexander, H. L. Frisch, Y. Kantor, K. Kremer, J. Percus, D. Stauffer, and T. Vicsek.

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