Continuum Percolation in an Interacting System: Exact Solution of the Percus-Yevick Equation for Connectivity in Liquids

Tony DeSimone,[a] Richard M. Stratt, and Sophia Demoulini[b]
Department of Chemistry, Brown University, Providence, Rhode Island 02912

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The general role of interparticle interactions is considered for percolation problems in liquids. With the aid of a diagrammatic formulation of the Percus-Yevick approximation, we analyze the dependence of connectedness (percolation) on correlation (interaction). This idea is illustrated by the analytical solution of the Percus-Yevick equation for a model of percolation in liquids, revealing that excluded volume (for example) may either enhance or suppress percolation.

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Because one is so often interested in the issue of connectivity in condensed-matter problems, the concepts of percolation theory[1,2] have found a wide range of applications. Metal-insulator transitions, cluster formation, and gelation are just a few examples of the types of uses to which percolation ideas have been put. However, while most of theoretical work in the area has been limited to crystal lattices, much of the experimental interest is in topologically disordered substances such as amorphous semiconductors or liquids.[3] Moreover, in examples such as the metal-insulator transition in expanded liquid metals,[4] the problem is not only a *continuum* problem but a *correlated* continuum problem—the interparticle interaction affects the probability of any two particles being connected. Thus the prototypical situation might be thought of as the one shown in Fig. 1.

Perhaps the first major contribution to the continuum problem, as such, was that of Scher and Zallen,[5] who suggested (by analogy to the "dimensional invariants" observed with different lattices) that there might be a certain critical volume fraction regardless of whether one was dealing with lattice or continuum percolation. Indeed, computer simulations seemed to bear out this idea.[6] But it was not until the recent development of formal diagrammatic theories for connectivity, analogous to the Mayer cluster expansion for correlation, that it became possible to think in any detail about how continuum percolation might differ from its lattice equivalent and specifically to consider the significance of the correlations that exist between the positions of particles in a liquid.[7-10] It is the aim of this Letter to show that the so-called Percus-Yevick approximation to the summation of the connectivity diagrams not only allows one to discuss the role of these correlations but also to solve a reasonably realistic model for percolation in liquids (that of Fig. 1) analytically.

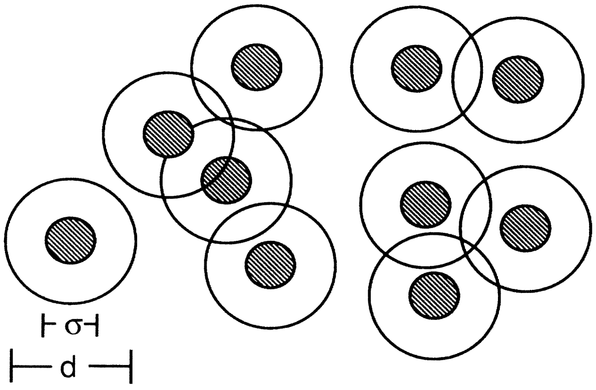

FIG. 1. Model of extended spheres: a fluid of molecules which *interact* with each other by virtue of their hard cores of diameter σ. Two molecules are assumed to be *connected* (capable of transferring electrons, for example) if their centers are within a distance d of each other. The percolation problem is thus to calculate the minimum density necessary to have a macroscopic fraction of the particles connected.

In the notation of Chiew, Glandt, and Stell,[8] the Boltzmann factor for two particles a distance r apart interacting through a potential $u(r)$, $e=\exp[-\beta u(r)]$, may be written as the sum of Boltzmann factors for connected, $e^\dagger=\exp[-\beta u^\dagger(r)]$, and disconnected, $e^*=\exp[-\beta u^*(r)]$, particles. Thus we may also write the Mayer f function, $f=e-1$, as the sum of connected, $f^\dagger=e^\dagger$, and disconnected, $f^*=e^*-1$, parts. For example, for the *extended sphere* problem of Fig. 1,

$$\begin{aligned} &f=-1, \quad f^\dagger=0, \quad f^*=-1, \quad r<\sigma; \\ &f=0, \quad f^\dagger=1, \quad f^*=-1, \quad \sigma<r<d; \qquad (1) \\ &f=0, \quad f^\dagger=0, \quad f^*=0, \quad r>d. \end{aligned}$$

Given these definitions it is straightforward to show that the diagrammatic series for the total pair correlation function (the density-density correlation function), $h(r)$, can itself be divided into connected and disconnected parts. The connected part, $h^\dagger(r)$, the conditional probability for finding a particle both a distance r away from a given tagged particle and connected to the tagged particle, satisfies the Ornstein-

Zernike–type equation

$$h^{\ddagger}(r_{12}) = c^{\ddagger}(r_{12}) + \rho \int d^3r_3\, c^{\ddagger}(r_{13})\, h^{\ddagger}(r_{32}), \qquad (2)$$

where ρ is the number density and $c^{\ddagger}$ is the direct connectedness function analogous to c, the direct correlation function of liquid theory.[11]

Equation (2), while exact, is hardly useful as it stands, but it becomes useful if an approximation such as the Percus-Yevick (PY) approximation is made for $c^{\ddagger}$. Even though this observation has been appreciated for some time,[7-9] it nonetheless turns out to be helpful to reformulate the PY approximation in an explicitly diagrammatic fashion. The PY approximation for classical liquids can be defined[11] by saying $c = fy$, where y, the cavity distribution function, is related to h by $h = (1+f)y - 1$. On substituting the expression for f in terms of $f^{\ddagger}$ and f^{*}, we derive the PY approximation for connectedness,

$$c^{\ddagger} = f^{*}y^{\ddagger} + f^{\ddagger}y. \qquad (3)$$

This equation, in combination with Eq. (2), the exact result

$$h^{\ddagger} = (1+f^{*})y^{\ddagger} + f^{\ddagger}y \qquad (4)$$

(which can be taken as a definition of $y^{\ddagger}$), and the standard methods of diagrammatic liquid theory,[11] allows us to give the following diagrammatic formulation of PY theory for connectedness:

$y^{\ddagger}(r_{12})$ = the sum of all simple diagrams composed of two white 1-circles labeled 1 and 2 (with no bond between them), one or more black ρ-circles, no articulation circles, and polygons of $f^{\ddagger}y$ bonds with interior decorations of f^{*} bonds that do not cross. (5)

As devotees of liquid theory will recognize, this series would be precisely the PY form for $y(r_{12})$ if all the bonds were f bonds.[12] However, Eq. (5), as written, not only lets us see the different roles of connecting and disconnecting bonds, but it also lets us see the effects of correlation: The presence of $f^{\ddagger}y = f^{\ddagger}(r)y(r)$ bonds means that the two-body connectivity, $f^{\ddagger}$, is renormalized by the pure interaction part of the problem. Note that $y(r)$ itself has the physical meaning of that part of the probability of finding two particles a distance r apart that is due to the explicitly many-body effects of the surrounding particles.[13] Thus we might predict that there may be fundamentally non-mean-field effects on percolation resulting from interparticle interaction.

We can understand the import of this general statement a little better if we consider the specific example of extended spheres defined by Eq. (1). Here one is simply trying to calculate the implications for the percolation process of an excluded volume (due to the finite size, σ, of the particles). With the aid of Eqs. (3) and (4), the associated mathematical problem reduces to the solution of Eq. (2) subject to the conditions

$$h^{\ddagger}(r) = 0, \quad r < \sigma, \qquad h^{\ddagger}(r) = y(r), \quad \sigma < r < d,$$

$$c^{\ddagger}(r) = 0, \quad r > d,$$

where $y(r)$ is now the Percus-Yevick cavity distribution function for hard spheres of diameter σ. For hard spheres, however, the definition of h in terms of y shows that we are just requiring $h^{\ddagger}(r) = g(r)$, $r < d$, where $g(r)$ is the Percus-Yevick radial distribution function $[h(r)+1]$ for hard spheres—a quantity known analytically.[14] The end result, somewhat surprising, is that the integral equation can be solved analytically by what is often called a Baxter factorization[15] over the range $\frac{1}{2} < \sigma/d < 1$. In this interval,[16] the direct connectedness function, $c^{\ddagger}(r)$, is piecewise polynomial in r.

In Fig. 2 we have plotted the resulting critical percolation density for this problem. This critical density was calculated from the requirement that the cluster size, the average number of particles connected to any given particle,

$$s = 1 + \rho \int d^3r\, h^{\ddagger}(r), \qquad (6)$$

diverges,[7] a condition equivalent, by virtue of Eq. (2), to requiring that the Fourier transform of $c^{\ddagger}$ at zero

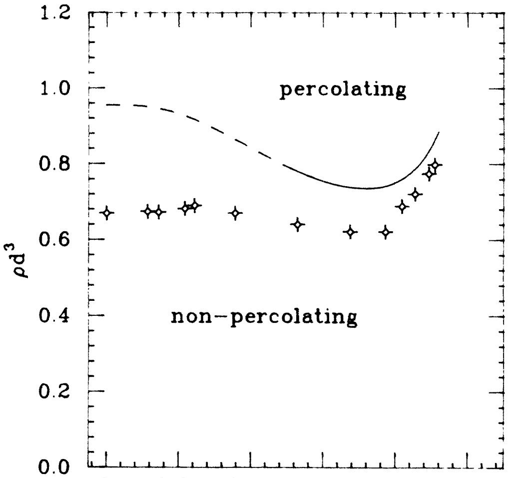

FIG. 2. The critical density for percolation of extended spheres, ρ, vs the hard-core diameter, σ (both in units of the connectedness distance d). The solid and dashed lines correspond to our analytical and numerical Percus-Yevick results, respectively. The points are from the Monte Carlo simulation of Ref. 17.

wave vector satisfy the equation $\rho \hat{c}^{\dagger}(0) = 1$. It is interesting to note some limiting cases of these formulas which have already been discussed in the literature. As σ/d approaches 0, the problem becomes that of *randomly centered spheres*[6-8]—continuum percolation with no interparticle interaction. On the other hand, as σ/d approaches 1, the problem approaches the impenetrable ($\epsilon \rightarrow 1$) limit of *permeable spheres*[8]—a somewhat phenomenological, but nonetheless intriguing, attempt at including excluded volume. Still, the portion of Fig. 2 relevant to real liquids is defined by $0 < \sigma/d < 1$, and it is there we see the most interesting behavior.

In distinct contrast both to the suggestion that the percolation density ought to be inversely proportional to excluded volume[18] and to the lattice-based notion that the density ought to be inversely proportional to coordination number,[1] we find a strongly nonmonotonic dependence on σ/d. Independent Monte Carlo results,[17] also shown in Fig. 2, nicely confirm our result. At large σ/d, the dependence is indeed consistent with what one would expect from coordination number arguments: As σ/d increases, the volume available for two particles to be connected ($\sigma < r < d$) decreases, decreasing the average coordination number and making percolation more difficult. At smaller σ/d, though, we propose that we are seeing several non-mean-field effects. One of these is a cage effect[13]: the genuinely many-body behavior common to liquids in which the particles surrounding two subject particles can hold them in proximity. Indeed, more detailed diagrammatic analysis shows that the inclusion of the hard-sphere cavity distribution function $y(r)$ in Eq. (5) always makes percolation easier. Even more important for an understanding of the minimum in the curve, perhaps, is the fact that, for a given cluster size [as defined by Eq. (6)], the presence of the hard core also serves to push the particles away from each other. Thus the *physical* extent of the clusters must increase as σ/d increases, even if the number of connected particles remains constant. Hence this effect will also make the density required to percolate decrease as σ/d increases. In fact, diagrammatically, the dip in the curve turns out to come solely from the interior decorations of f^* bonds—which represent just this exclusion of volume around a sphere.[16]

It should still be emphasized that the Percus-Yevick approximation is not as accurate for connectedness as it is for correlation (for reasons which can be understood diagrammatically[16]). As illustrated in Fig. 2, the numerical values for ρd^3 become quantitatively accurate only for large σ/d.[17,19] The basic idea revealed by the approximation remains, however: Interparticle interaction has noticeable ramifications for percolation in liquids. At the very least, this finding suggests that scaling arguments will need to take into account the roles of *both* connectedness and correlation length scales.[10]

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[a] Permanent address: Department of Physics, Brown University, Providence, R.I. 02912.

[b] Present address: Department of Mathematics, Purdue University, West Lafayette, Ind. 47907.

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[19] For $\sigma/d = 0$ we calculate $\rho d^3 = 3/\pi = 0.955$, whereas the series expansion of Hahn and Zwanzig (Ref. 7) gives $\rho d^3 = 0.669$. Of more fundamental interest, though, is the fact that the PY approximation does not predict hard-sphere freezing. We (in agreement with Ref. 8) would expect ρd^3 *not* to diverge at $\sigma/d = 1$, but, rather, to give percolation at a density lower than that of random close packing ($\rho\sigma^3 \cong 1.2$).