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Percolation behaviour of permeable and of adhesive spheres

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Abstract. The pair-connectedness function and the average cluster size are determined for two different three-dimensional fluid systems using the Percus–Yevick (PY) approximation. The permeable-sphere model of Blum and Stell provides a one-parameter bridge from the ideal gas (perfectly penetrable spheres) to the PY hard-sphere fluid. Two of such particles are considered to be 'bound' when their cores overlap. The percolation transition is located as a function of the interpenetrability of the particles, and is found to correspond to an average coordination number $\bar{z} = 4$. Baxter's adhesive-sphere model is also investigated in the PY approximation and it is found that at the percolation transition the average coordination number is 2. The boundary between percolating and non-percolating homogeneous thermodynamic states is determined.

1. Introduction

Percolation or connectivity concepts are a subject common to a variety of problems involving the determination of macroscopic properties which are strongly affected by the existence of an infinite cluster. Thus, percolation theory has been used in the study of conduction in disordered materials (Kirkpatrick 1973, 1979), of gelation (Coniglio *et al* 1982) and of the structure of liquid water (Stanley and Texeira 1980). In addition to the percolation transition, the theory provides information on cluster statistics relevant to many physical systems.

An effort has been made in recent years towards an understanding of the relationship between percolation transitions and thermal phase transitions, and in applying these ideas to other phenomena in disordered systems. These works are described in recent reviews (Stauffer 1979, Essam 1980). Most of such studies have been on lattice systems. The study of percolation in a continuum has received comparatively less attention. For example, series expansions (Haan and Zwanzig 1977) and Monte Carlo studies (Gawlinski and Stanley 1981, Vicsek and Kertesz 1981) have been reported for the latter case. Furthermore, almost all such studies are concerned with systems of non-interacting particles, where the concept of connectivity is equivalent to that of overlap. The percolation behaviour in these cases is independent of temperature.

The present work is concerned with continuous percolation in systems of particles whose configuration obeys a Gibbsian distribution according to two different models for the interparticle potential. The first of these models is the system of permeable or partly penetrable spheres proposed by Stell and coworkers (Blum and Stell 1979, 1980, Salacuse and Stell 1982). It consists of a one-parameter family of structures which has as its two extremes (i) the ideal gas, i.e. a fluid of perfectly non-interacting particles, and (ii) the hard-sphere fluid in the Percus–Yevick (PY) approximation. The intermediate values of the parameter correspond to varying degrees of core inter-penetrability. The temperature of the fluid need not be defined explicitly, but the degree of penetrability of the spheres can be regarded as a dimensionless indication of its value. The second kind of system for which we investigate the percolation behaviour is the adhesive-sphere model of Baxter (1968a). It describes an assembly of particles with a spherical hard core plus an attractive interaction which is infinitely short-ranged. In addition to its density, an adhesive-sphere fluid is characterised by a reduced temperature τ. Its inverse is interpreted as the interparticle adhesiveness. The limit $\tau \to \infty$ corresponds to a system of hard spheres.

2. Physical clusters and pair connectedness

The study of the distribution of physical clusters in an equilibrium system of interacting particles requires an arbitrary separation of the Boltzmann factor into two parts (Hill 1955)

$$\exp[-\beta u(r)] = \exp[-\beta u^+(r)] + \exp[-\beta u^*(r)] \tag{1}$$

where $u^+(r)$ and $u^*(r)$ are the interaction potentials for bound and unbound pairs of particles, respectively. The corresponding Mayer f-functions are defined as

$$f^+(r) = \exp[-\beta u^+(r)], \qquad f^*(r) = \exp[-\beta u^*(r)] - 1. \tag{2a, b}$$

The pair-connectedness function $P(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is defined so that $\rho^2 P(\boldsymbol{r}_1, \boldsymbol{r}_2)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2$ is the probability of simultaneously finding a particle in $\mathrm{d}\boldsymbol{r}_1$ at $\boldsymbol{r}_1$ and another particle, of the same cluster, in $\mathrm{d}\boldsymbol{r}_2$ at $\boldsymbol{r}_2$. In an isotropic system $P(\boldsymbol{r}_1, \boldsymbol{r}_2) = P(r_{12})$. Coniglio *et al* (1977a) derived the cluster expansion for $P(r)$ by replacing every f-bond in the corresponding expansion for the pair-correlation function with the sum $f(r) = f^+(r) + f^*(r)$. The pair-connectedness function $P(r)$ can then be identified with the collection of diagrams having at least one unbroken path of f^+-bonds connecting the root points 1 and 2. The graphs in $P(r)$ can be divided into the nodal or bridge graphs $b^+(r)$ and the direct or non-nodal graphs $C^+(r)$. An Ornstein–Zernike relation can be established between $P(r)$ and $C^+(r)$:

$$P(r) = C^+(r) + \rho \int C^+(r')P(|\boldsymbol{r} - \boldsymbol{r}'|)\,\mathrm{d}\boldsymbol{r}'. \tag{3}$$

The PY approximation

$$g(r) = \exp[-\beta u(r)][1 + b(r)], \tag{4}$$

where $b(r)$ is the nodal part of the pair-correlation function $g(r)$, is one of the most convenient and widely used closures for the Ornstein–Zernike integral equation. It can also be suitably modified for the connectedness problem by the introduction of equation (2). The result is (Coniglio *et al* 1977a)

$$P(r) = \exp[-\beta u^+(r)]g(r)\exp[\beta u(r)] + \exp[-\beta u^*(r)][P(r) - C^+(r)]. \tag{5}$$

The system of equations (3) and (5) must be solved for both $P(r)$ and $C^+(r)$. The mean cluster size S can be computed from the analogue of the compressibility equation

$$S = 1 + \rho \int P(r)\,\mathrm{d}\boldsymbol{r} \tag{6}$$

with the percolation threshold ρ_p corresponding to the limit $S \to \infty$.

3. The permeable-sphere system

The permeable-sphere model was proposed by Blum and Stell (1979, 1980) as a generalisation of the hard-sphere model. The PY approximation is imposed outside the core

$$c(r) = 0 \qquad \text{for } r > d \tag{7}$$

whereas the usual hard-core condition is modified to

$$g(r) = 1 - \varepsilon \qquad \text{for } r < d. \tag{8}$$

The parameter ε is a measure of the mutual impenetrability of the particles. Thus, $\varepsilon = 0$ corresponds to the ideal gas, and $\varepsilon = 1$ to the PY hard-sphere case. Stell and coworkers pointed out that this model enjoys a significant property: the solution to the Ornstein–Zernike equation for a number density ρ can be expressed directly in terms of the corresponding hard-sphere solution for the density $\varepsilon\rho$,

$$g(r; \rho, \varepsilon) = \varepsilon g^{\mathrm{HS}}(r; \varepsilon\rho) + 1 - \varepsilon. \tag{9}$$

The effective (density-dependent) interparticle potential equivalent to (7) and (8) can be computed in a straightforward manner as

$$u(r) = -kT \ln \frac{1-\varepsilon}{1-\varepsilon[1+c^{\mathrm{HS}}(r)]} \tag{10}$$

where $c^{\mathrm{HS}}(r)$ is the PY direct correlation function for the hard-sphere system (Salacuse and Stell 1982).

The percolation transition of a permeable-sphere system will depend on the parameter ε. In this case the natural definition of a bound pair is that of particles with core overlap, so that in (1)

$$\exp[-\beta u^{+}(r)] = \frac{1-\varepsilon}{1-\varepsilon[1+c^{\mathrm{HS}}(r)]}, \qquad r < d, \tag{11a}$$

$$= 0, \qquad r > d, \tag{11b}$$

$$\exp[-\beta u^{*}(r)] = 0, \qquad r < d, \tag{12a}$$

$$= 1, \qquad r > d. \tag{12b}$$

With this separation, (5) becomes

$$P(r) = g(r), \qquad r \leq d, \tag{13}$$

$$C^{+}(r) = 0, \qquad r > d. \tag{14}$$

4. Percolation in the permeable-sphere model

The short-range nature of $C^+(r)$ makes it appropriate to solve the Ornstein–Zernike equation (3) through the application of the method due to Baxter (1968b). It amounts to a transformation of the original integral equation into the following two relations, written here in the language of the pair-connectedness problem:

$$rC^+(r) = -q'(r) + 2\pi\rho \int_r^d q'(t)q(t-r)\,\mathrm{d}t, \qquad 0<r<d, \tag{15}$$

$$rP(r) = -q'(r) + 2\pi\rho \int_0^d (r-t)P(|r-t|)q(t)\,\mathrm{d}t, \qquad r>0, \tag{16}$$

where $q(r)$ has the property

$$q(r) = 0 \qquad \text{for } r<0 \text{ and } r>d. \tag{17}$$

When (8) and (13) are introduced into (16) we obtain, for the range $0<r<d$,

$$q'(r) = \alpha r + \beta \tag{18}$$

where α and β are constants given by

$$\alpha = -(1-\varepsilon) + (1-\varepsilon)2\pi\rho \int_0^d q(t)\,\mathrm{d}t, \tag{19}$$

$$\beta = -(1-\varepsilon)2\pi\rho \int_0^d tq(t)\,\mathrm{d}t. \tag{20}$$

On integration of (18) and application of the boundary condition of (17), α and β are found to be

$$\alpha = \frac{(1-\varepsilon)[2\eta(1-\varepsilon)-1]}{[1+(1-\varepsilon)\eta]^2}, \qquad \beta = \frac{-\frac{3}{2}\eta(1-\varepsilon)^2}{[1+(1-\varepsilon)\eta]^2}, \tag{21a, b}$$

while

$$q(r) = \tfrac{1}{2}\alpha(r^2-d^2) + \beta(r-d) \tag{22}$$

where we have defined $\eta = \pi\rho d^3/6$. This quantity does not correspond to the volume fraction of the spheres, except in the hard-particle limit of $\varepsilon = 1$.

Following Baxter's method (1968b) we define the function $\tilde{Q}(k)$ by

$$\tilde{Q}(k) = 1 - 2\pi\rho \int_0^d \mathrm{e}^{\mathrm{i}kr} q(r)\,\mathrm{d}r \tag{23}$$

which is related to the pair-connectedness function by

$$1 + \rho\tilde{P}(k) = [1-\rho\tilde{C}^+(k)]^{-1} = [\tilde{Q}(k)\tilde{Q}(-k)]^{-1} \tag{24a, b}$$

where $\tilde{P}(k)$ and $\tilde{C}^+(k)$ are the Fourier transforms of $P(r)$ and $C^+(r)$, respectively. Thus, the mean cluster size S of (6) is

$$S = 1 + \rho\tilde{P}(0) = [1-\rho\tilde{C}^+(0)]^{-1} = [\tilde{Q}(0)]^{-2} \tag{25a, b, c}$$

and the result is

$$S(\varepsilon, \eta) = [1+\eta(1-\varepsilon)]^4/[2\eta(1-\varepsilon)-1]^2. \tag{26}$$

The percolation transition corresponds to the divergence in S:

$$\eta_p = 1/2(1-\varepsilon). \tag{27}$$

Equation (27) is plotted in figure 1. In the limit of $\varepsilon = 0$, the fully permeable or ideal gas case is recovered, and it is seen that the value of the percolation threshold is predicted to be $\eta_p = \frac{1}{2}$. The mean cluster size diverges with the exponent $\gamma_p = 2$. Table 1 shows a comparison of these results with the previously reported Monte Carlo and series expansion figures. The poor agreement is undoubtedly due to the use of the PY approximation in the present calculations. However, the PY solution permits the easy computation of the pair-connectedness function by a numerical integration of (16). Such a function is represented in figure 2, for the ideal-gas case, for various values of the reduced number density $\rho^* = \rho d^3$. The corresponding particle volume fractions are simply given by $\phi = 1 - \exp(-\pi\rho^*/6)$. As should be expected, $P(r)$ is unity for $r < d$, is discontinuous at $r = d$ and decreases monotonically for $r > d$.

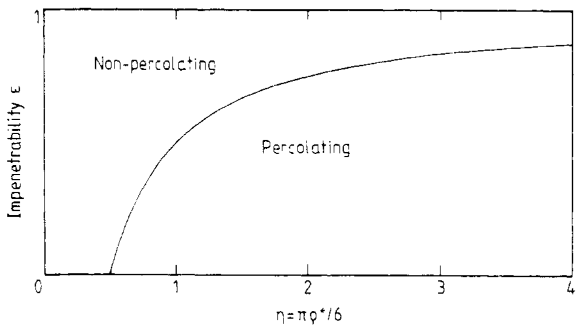

Figure 1. PY approximation to the percolation transition for permeable spheres. The parameter ε is a measure of the mutual impenetrability of the particles.

Table 1. Estimated critical percolation density and critical exponent γ_p for fully penetrable spheres.

$\eta_p = \pi\rho_p d^3/6$		γ_p, exponent for the mean cluster size	
Domb (1972)	0.339	Haan and Zwanzig (1977)	1.80 ± 0.2
Fremlin (1976)	0.388 ± 0.013	Present work	2.0
Gayda and Ottavi (1974)	0.325 ± 0.013		
Haan and Zwanzig (1977)	0.35 ± 0.03		
Holcomb *et al* (1972)	0.293		
Kurkijarvi (1974)	0.347 ± 0.011		
Present work	0.5		

When the PY approximation is applied to hard spheres, it is unable to reproduce either the equilibrium fluid–solid transition or to evidence any irregularities associated with random-close packing phenomena. The connectivity behaviour in this limit is equally unphysical. The predicted percolation transition occurs at $\eta_p \to \infty$, while it should be expected that the actual value for a disordered system should coincide with the random packing figure of $\eta \simeq 0.63$.

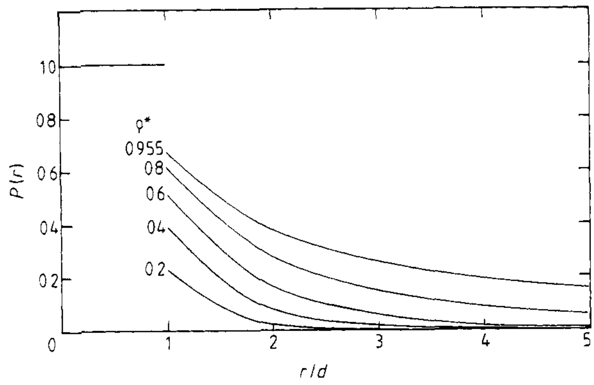

Figure 2. Pair-connectedness function for the ideal-gas system.

The pair-connectedness functions for several intermediate cases of limited permeability are displayed in figure 3 for a fixed number density $\rho^* = 0.8$. The overall behaviour is similar to that of the ideal gas but with $P(r) = 1 - \varepsilon$ inside the core. At this density the hard-sphere limit $\varepsilon \to 1$ is $P(r) = 0$ for all r.

The average coordination number of the particles is immediately computable as

$$\bar{Z} = \int_0^d 4\pi r^2 \rho P(r)\,\mathrm{d}r. \tag{28}$$

At the percolation transition this number is $\bar{Z}_\mathrm{p} = 4$. This result applies to all values of the degree of impenetrability parameter ε.

5. The adhesive-sphere system

This is a model proposed by Baxter (1968a). The pair potential is defined by

$$\beta u(r) = \begin{cases} +\infty, & 0 < r < \sigma, & (29) \\ -\ln\left[\dfrac{d}{12\tau(d-\sigma)}\right], & \sigma < r < d, & (30) \\ 0, & r > d, & (31) \end{cases}$$

in the limit $\sigma \to d$. Thus, the Boltzmann factor develops a Dirac delta contribution at contact

$$\exp[-\beta u(r)] = (d/12\tau)\delta(r-d), \qquad r \leqslant d, \tag{32}$$

$$= 1 \qquad r > d. \tag{33}$$

Here τ is a dimensionless indicator of the temperature; the exact correspondence can be regarded as arbitrary. Thus, the quantity τ^{-1} is a measure of the stickiness of the particles, with $\tau^{-1} \to 0$ corresponding to non-sticky hard spheres.

Baxter (1968a) obtained analytic results for this model in the PY approximation. He found the radial distribution function within the core to be

$$g(r) = \tfrac{1}{12}\lambda d\delta(r-d), \qquad 0 < r \leqslant d. \tag{34}$$

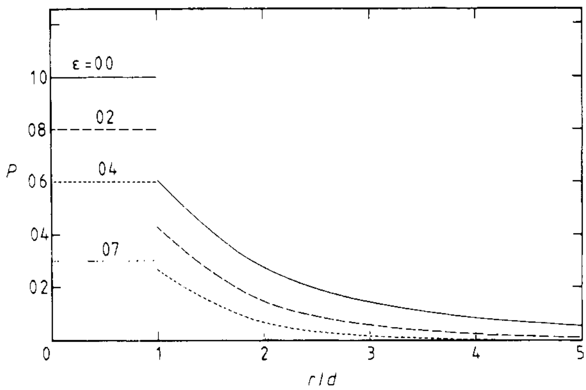

Figure 3. Pair-connectedness function for permeable spheres at a reduced density $\rho^* = \rho d^3 = 0.8$.

Unlike in the case of hard spheres, (34) yields a finite probability of finding pairs of particles in contact at $r = d$. In fact, the average coordination number is

$$\bar{Z} = 2\lambda\eta. \tag{35}$$

As before, $\eta = \pi\rho d^3/6$, but it can now be identified with the volume fraction of particles. The dimensionless parameter λ is related to τ and η by

$$\frac{\eta}{12}\lambda^2 - \left(\frac{\eta}{1-\eta} + \tau\right)\lambda + \frac{1+\eta/2}{(1-\eta)^2} = 0 \tag{36}$$

where only one of the roots is physically significant. Baxter (1968a) has shown that this system undergoes a first-order liquid–vapour transition. The coexistence curve was obtained by Watts *et al* (1971) using the energy-equation route to the equation of state.

The physical-cluster distribution and percolation behaviour of an adhesive-sphere system will depend on the parameter τ. The natural definition of bound neighbours, as in (1), is that of particles at contact, so that

$$\exp[-\beta u^+(r)] = (d/12\tau)\delta(r-d) \qquad \text{for all } r, \tag{37}$$

$$\exp[-\beta u^*(r)] = 0 \qquad \text{for } 0 < r < d, \tag{38}$$

$$= 1 \qquad \text{for } r < d. \tag{39}$$

6. Percolation in the adhesive-sphere model

Equations (13) and (14) are also applicable in this case. The same procedure as with penetrable spheres can be followed to yield the obvious result

$$P(r) = \tfrac{1}{12}\lambda d\delta(r-d) \qquad \text{for } 0 < r \leqslant d. \tag{40}$$

Again, (16) can be integrated numerically to yield the full pair-connectedness function. Figure 4 displays the pair-correlation functions (upper curves) and pair-connectedness functions (lower curves) for three thermodynamic states. All six curves include a singular contribution given by (40). Also, figure 5 shows the pair-connectedness

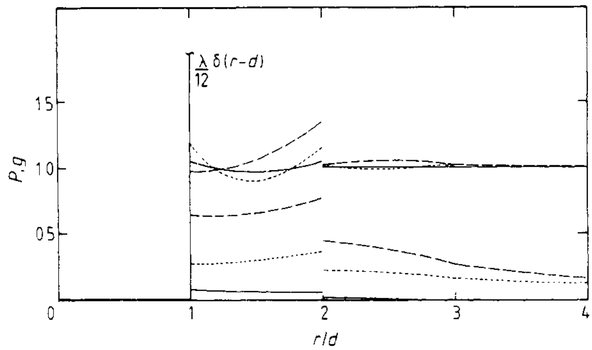

Figure 4. Pair-correlation (upper three) and pair-connectedness (lower three) curves for the adhesive-sphere fluid. ——: $\eta = 0.1$, $\tau = 0.35$ ($\lambda = 2.971$); ------: $\eta = 0.29$, $\tau = 0.35$ ($\lambda = 3.35$); - - -: $\eta = 0.1$, $\tau = 0.11$ ($\lambda = 8{\cdot}745$).

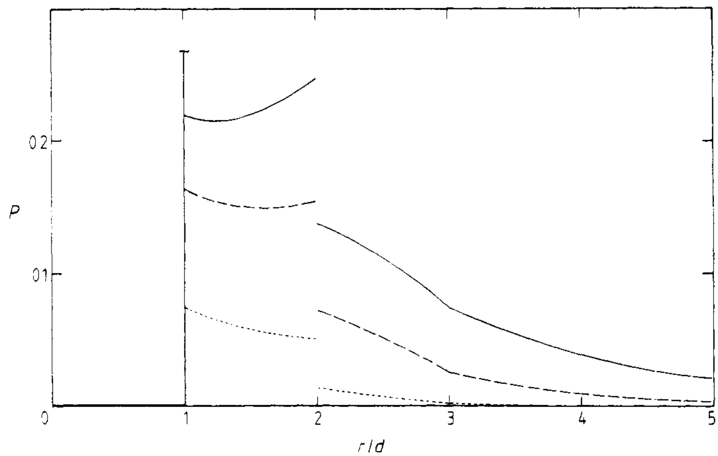

Figure 5. Pair-connectedness function for an adhesive-sphere system at $\tau = 0.35$. ——: $\eta = 0.25$ ($\lambda = 3.249$); - - -: $\eta = 0.2$ ($\lambda = 3.138$); ------: $\eta = 0.1$ ($\lambda = 2.971$).

functions for three systems at the same temperature, while figure 6 does the same for three systems of equal density. All the curves are discontinuous at $r = 2d$, as $g(r)$ is, and their successively higher derivatives become discontinuous at successively higher multiples of d (Cummings *et al* 1976).

Following the same procedure as in § 5, the mean cluster size is found to be

$$S = 1/(1-\lambda\eta)^2 \tag{41}$$

so that the percolation transition corresponds to

$$\eta = 1/\lambda \tag{42}$$

which, when combined with (36), yields the locus of the percolation line on the τ–η plane

$$\tau = (19\eta^2 - 2\eta + 1)/12(1-\eta)^2. \tag{43}$$

Baxter (1968a) has shown that there is a region in the τ–η plane which corresponds

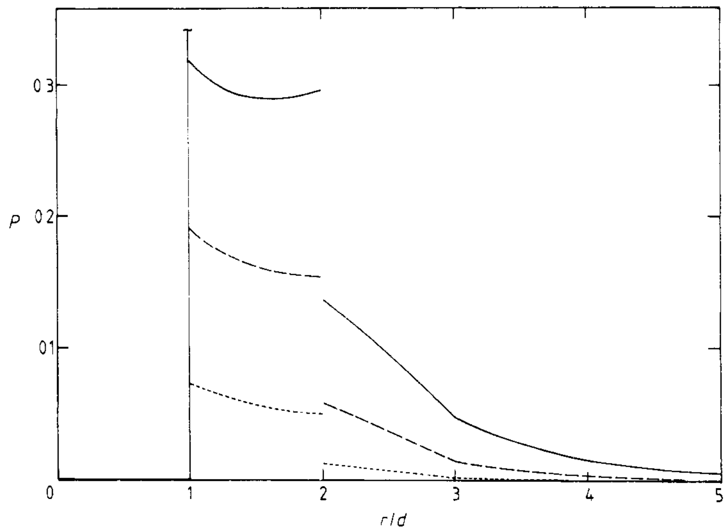

Figure 6. Pair-connectedness function for an adhesive-sphere system at $\eta = 0.1$. ——: $\tau = 0.15$ ($\lambda = 6.186$); - - -: $\tau = 0.2$ ($\lambda = 4.778$); ------: $\tau = 0.35$ ($\lambda = 2.971$).

to unphysical values of λ (see also Watts *et al* 1971). It should be noted that the percolation line lies entirely outside this region.

It is of great interest to examine the relation between percolation and thermal phase transitions for the same system (Coniglio *et al* 1977a, b). Baxter (1968a) showed that the adhesive-sphere model exhibits a first-order liquid–gas transition, and used the compressibility equation to locate the critical point at $\eta_c = 0.1213$, $\tau_c = 0.0976$. Watts *et al* (1971) improved upon this estimate by obtaining the coexistence curve, shown in figure 7. Their results for the critical point are $\eta_c = 0.32$, $\tau_c = 0.1185$. The

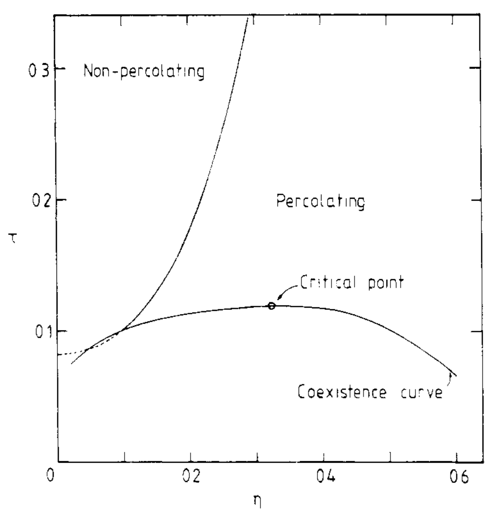

Figure 7. Coexistence and percolation lines for the adhesive-sphere model fluid. The coexistence line was obtained by Watts *et al* (1971) using the PY energy-equation approach.

PY coexistence and percolation lines do not meet at the critical point in figure 7, as would have been expected of a two-dimensional case (Coniglio *et al* 1977b). Jointly, they divide the thermodynamic plane into percolating and non-percolating states. The significance of the continuation of the percolation line into the two-phase region is yet to be elucidated.

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