Tests of Universality of Percolation Exponents for a Three-Dimensional Continuum System of Interacting Waterlike Particles

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Molecular-dynamics calculations for *interacting* waterlike particles are used to estimate values of percolation exponents. Results are consistent with accepted values for ordinary *random*-bond percolation for a three-dimensional lattice. Study of a correlated-site percolation problem, defined by the connectivity of those water molecules that are four-coordinated, shows no evidence for different exponents. Thus there is no obvious basis for the frequent criticisms against the application of lattice percolation models to describe *continuum correlated* systems such as polymer gels.

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Are the critical properties of *interacting* three-dimensional continuum systems the same as those known for *noninteracting* models in which the particles are constrained to the vertices of a lattice? This question has arisen recently as percolation is being used increasingly to describe an ever wider range of natural phenomena—ranging from gelation of polyfunctional monomers to the hydrogen-bond network in liquid water.[1-3] Unfortunately, all calculations of critical exponents for three-dimensional systems have been for *random* systems—there have been no calculations of the critical exponents for an *interacting* continuum three-dimensional system.[4] Even the simpler case of a continuum two-dimensional system is just beginning to be studied with sufficient accuracy that critical exponents can be obtained.[5] Liquid water is one of the most intensely studied continuum systems for which association of individual constituents plays an important role. In this work we analyze a molecular-dynamics simulation of a model of liquid water to obtain exponents for a three-dimensional continuum system whose elements are *not* random.

The input to the present work is a computer tape[6] resulting from a molecular-dynamics simulation of a system consisting of 216 particles confined to a cubic box of edge 18.6 Å with periodic boundary conditions (density 1 g/cm^3); the temperature of the system was 284 K. The particles interact through an ST2 effective pair potential designed to reproduce a wide range of properties of real water. Its most prominent feature is a tetrahedral charge distribution around the oxygen atom, with two positive partial charges on the proton location and two negative partial charges representing the lone electron pairs. The absolute minimum of the ST2 potential is −6.84 kcal/mole.

The Stillinger-Rahman tape consists of a simulation with 38 100 time steps. After each 300 steps, we created a 216×10 table containing for each molecule i ($i = 1, 2, \ldots, 216$) the ten other molecules j that interact most strongly in an attractive way with molecule i. We thereby obtain a set of 127 (= 38 100/300) different tables, which are then used as input for the following procedure to calculate the time-averaged cluster size distributions.

We use two definitions of a hydrogen bond: Definition D_1 defines hydrogen bonds by a purely energetic criterion.[7] Specifically, molecules i and j are considered to be "bonded" if their pair interaction energy satifies $V_{ij} < V_{HB}$. The parameter V_{HB} is permitted to take on a sequence of 32 discrete values $V_{HB} = -20E, -22E, \ldots, -82E$, where $E = 0.075\,75$ kcal/mole. Clearly $V_{HB} = -20E$ represents the most permissive definition of a hydrogen bond, while $V_{HB} = -82E$ is the least permissive definition. In the case of permissive definitions, there sometimes occur water molecules having more than four bonds; in this case we eliminate the weakest "extra" bonds in the system until there are a maximum of four bonds per molecule.

It may be argued that a purely energetic criterion includes in the list of bonded partners pairs

of molecules that have an interparticle separa-
tion that is too large for a hydrogen bond; more-
over the elimination of extra bonds introduces
some ambiguity. Therefore in definition D_2 we
add a *geometric* cutoff and eliminate from the
list of strongly interacting partners of molecule
i all molecules j whose separation $|r_i - r_j|$ ex-
ceeds 3.5 Å, but we do not eliminate any extra
bonds. Also, to get better statistics, we gen-
erated 800 tables by analyzing after every forty
time steps.

Thus, given a configuration of water molecules,
we get for each water molecule i a list of its
directly bonded partners $j, k, \ldots$. These lists
allow us to construct "bond clusters" of mole-
cules such that stepping along successive hydro-
gen bonds keeps us confined to a given "bond
cluster." An illustrative example is given in
Appendix A of Ref. 8. For each "snapshot" of
the system, we calculate W_s, the number of
water molecules belonging to a bond cluster with
s molecules. Thus W_1 is the number of unbonded
molecules, W_2 the number of water molecules
belonging to two-molecule clusters, and so forth.
In the language of percolation theory this is the
bond percolation problem with *site counting*;
note that exact enumeration procedures for bond
percolation usually employ *bond counting*.[9]

If we reexamine the same configurations but
now eliminate all molecules with less than four
intact bonds, we obtain a correlated-site percola-
tion problem[10,11] that is believed to have the same
exponents as random percolation.[12,13] The num-
ber of molecules belonging to a cluster of s "four-
bonded" molecules is denoted W_s^*. Molecules
with more than four bonds (using definition D_2)
are added to the class of four-bonded molecules
in the following.

In order that systems with differing numbers of
particles can easily be compared, it is convenient
to normalize the cluster distribution by N (= 216),
the total number of particles. Thus $w_s(V_{HB})$
$= N^{-1} W_s(V_{HB})$ is the fraction of water molecules
belonging to a bond cluster of s molecules, with
an analogous definition for w_s^*. For each value
of V_{HB}, we also calculate the total number of
hydrogen bonds in the entire system, N_{HB}. Again
we normalize by the total number of particles,
so that $n_{HB}(V_{HB}) = 2N^{-1}N_{HB}(V_{HB})$ is the mean num-
ber of hydrogen bonds per molecule. For the 32
values of V_{HB} given above, n_{HB} takes on a corre-
sponding set of 32 values ranging from 0.08 to
3.59 for D_1 and from 0.08 to 4.06 for D_2. Since
there is a 1:1 relation between V_{HB} and n_{HB}, it

is convenient to think of the weight fractions w_s
as functions of n_{HB}.

For each value of V_{HB}, we have calculated the
cluster distributions w_s and w_s^* and obtained the
following additional "averaged" quantities:

(i) Mean cluster size. The mean cluster size
of the finite networks, S, is conventionally de-
fined as the average of s with respect to the dis-
tribution function w_s, $S = \sum' s w_s / \sum' w_s$. The
primes indicate that the spanning networks are
omitted from the sums, i.e., clusters that cross
the entire box in at least one coordinate direction
are eliminated. Defining $\epsilon \equiv (p_c - p)/p_c$, with p
$\equiv n_{HB}/4$, we expect $S \sim C\epsilon^{-\gamma}$. Figure 1 shows
double logarithmic plots of S and S^* (the asterisk,
throughout, denotes the continuum correlated-site
problem defined by the four-bonded molecules).
The straight lines have slope 1.7, and are seen
to fit the data which are close to the percolation
threshold, but not so close that rounding effects
arise as a result of the finite system size. Thus
we find that γ and γ^* are consistent with the lat-
tice estimates $\gamma = 1.73 \pm 0.3$.[14] We also find values
of p_c consistent with the ice lattice values p_c
$= 0.388$,[9,15] and $p_c^* = 0.795$.[16] This fact is some-
what surprising, since one might expect expo-
nents to be universal but not necessarily the val-
ue of the threshold parameter p_c.

(ii) Order parameter. For finite systems, the
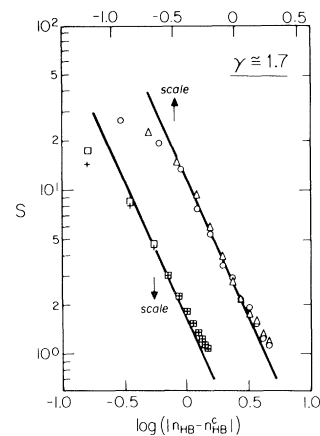fraction of molecules belonging to spanning clus-

FIG. 1. Mean cluster size S for bond networks de-
termined by bond definitions D_1 (squares) and D_2 (cros-
ses). Also shown are the corresponding quantities for
D_1 (circles) and D_2 (triangles) for clusters of four-
bonded water molecules. The straight line shown is
drawn through the steepest part of the curve, since
there is rounding for small values of ϵ and crossover
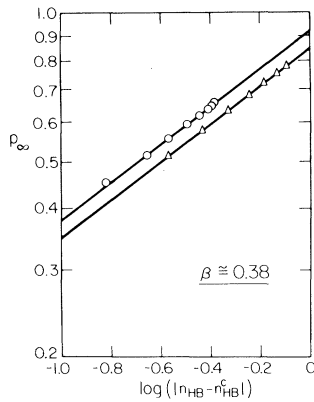to mean-field value $\gamma = 1$ for large values of ϵ.

FIG. 2. Order parameter P_∞ for clusters of four-bonded water molecules with use of both bond definitions D_1 (circles) and D_2 (triangles).

FIG. 3. Average length L determined by definition D_1 for both bond networks (squares) *and* clusters of four-bonded water molecules (circles). The normalization factor 2.82 Å is roughly the length of a typical hydrogen bond.

ters is regarded as the order parameter, denoted P_∞. As the system size becomes infinite, we expect that $P_\infty = B\epsilon^\beta$, thereby defining the exponent β and the amplitude B. For lattice percolation, $\beta = 0.42 \pm 0.06$,[17] while from analysis of our correlated-site percolation data (Fig. 2) we find $\beta = \beta^* = 0.38 \pm 0.05$. The amplitude B differs by 8% for the two bond definitions.

(iii) *Characteristic length.* The length L_s of an s-molecule cluster is defined as the difference between the maximum and minimum oxygen coordinates of the cluster (with respect to some chosen coordinate direction). To get better statistics, all three Cartesian coordinate directions have been used successively. Since the length of a one-molecule cluster is zero, only clusters with $s > 1$ have been treated. Also, only nonspanning clusters are considered. Figure 3 is a double-logarithmic plot showing the dependence of the averages over all clusters L and L^* on ϵ; the slope is 0.75 ± 0.1, consistent with literature estimates of the exponent ν in $L_s \sim A\epsilon^{-\nu}$ for lattice percolation.[14,18-20] Unlike most calculations, we can *also* obtain the amplitude A, with the results $A = 1.0$ Å and $A^* = 1.5$ Å.

(iv) *Weight fraction w_s of clusters of size s.* At p_c the weight fraction of clusters of size s is expected to decrease with s as $w_s \sim s^{-(\tau-1)}$, where $\tau = 2 + 1/\delta$; $\delta = 5.0 \pm 0.1$ for lattice percolation.[21] Figure 4 shows w_s and w_s^* averaged over those values of p_B closest to the threshold. The straight line has slope 1.2 and is seen to pass through even the data point for $s = 2$. Actually the data set of w_s for $n_{HB} = 1.55$, being very close to the
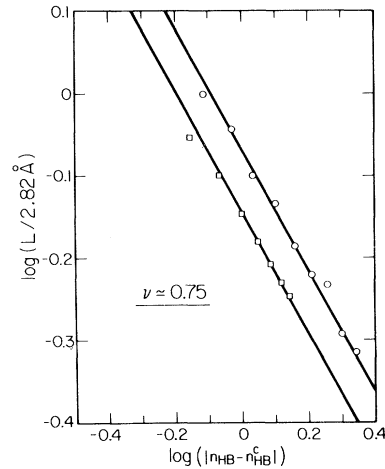
threshold $n_{HB}{}^c$, showed rather large fluctuations as expected from lattice calculations.[22]

In summary, we have estimated the exponents β, γ, ν, and $\tau = 2 + 1/\delta$ for a continuum interacting system in three dimensions. Our estimates for all four exponents are consistent with the estimates for a lattice system. Thus there is no ob-
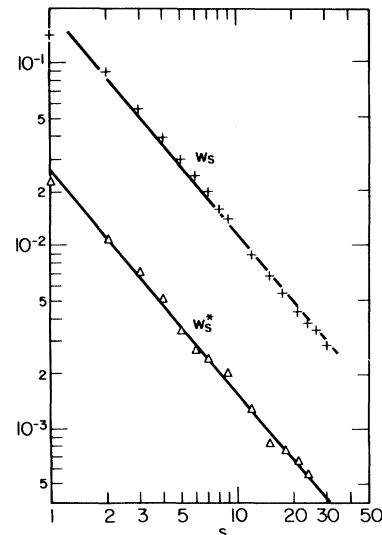

FIG. 4. Weight fraction of molecules belonging to clusters of size s determined by definition D_2 for both bond networks (crosses) and four-bonded water molecules (triangles). The straight lines have slope 1.2, since $\tau - 1 = 1 + \delta^{-1}$.

vious reason to doubt the application of *random, lattice* percolation to describe the connectivity properties of *interacting, continuum* systems such as polymer gels and water.[1-3]

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[1]Percolation is reviewed by D. Stauffer, Phys. Rep. 54, 1 (1979).

[2]For applications to gelation, see D. Stauffer, A. Coniglio, and M. Adam, Adv. Polym. Sci. 44, 103 (1982).

[3]For applications to liquid water, see C. A. Angell, to be published.

[4]There does exist some work on continuum percolation in three dimensions [see, e.g., R. Zallen and H. Scher, Phys. Rev. B 4, 4471 (1971)]. Estimates of critical exponents are generally not attempted, with the exception of I. Webman, J. Jortner, and M. H. Cohen, Phys. Rev. B 14, 4737 (1976), who calculate the conductivity exponent t.

[5]Specifically, S. W. Haan and R. Zwanzig, J. Phys. A 10, 1547 (1977), estimated γ for a system of $d = 2$ penetrable (noninteraction) disks, using series methods. T. Vicsek and J. Kertész, J. Phys. A 14, L31 (1981), estimated ν for the same system with Monte Carolo renormalization group, while E. T. Gawlinski

and H. E. Stanley, J. Phys. A 14, L291 (1981), estimated β, γ, ν, and τ, using Monte Carlo methods. Very recently, E. T. Gawlinski and S. Redner, J. Phys. A (to be published), have considered the effect of a hard-core interaction in $d = 2$ continuum systems.

[6]F. H. Stillinger and A. Rahman, J. Chem. Phys. 60, 1545 (1974).

[7]A. Rahman and F. H. Stillinger, J. Chem. Phys. 55, 3336 (1971).

[8]A. Geiger, F. H. Stillinger, and A. Rahman, J. Chem. Phys. 70, 4185 (1979).

[9]See, e.g., M. F. Sykes, D. S. Gaunt, and M. Glen, J. Phys. A 9, 1705 (1976).

[10]H. E. Stanley, J. Phys. A 10, L211 (1979); H. E. Stanley and J. Teixeira, J. Chem. Phys. 73, 3404 (1980).

[11]H. E. Stanley, J. Teixeira, A. Geiger, and R. L. Blumberg, Physica (Utrecht) 106A, 260 (1981).

[12]R. L. Blumberg, G. Shlifer, and H. E. Stanley, J. Phys. A 13, L147 (1980).

[13]A. E. Gonzalez and P. J. Reynolds, Phys. Lett. 80A, 357 (1980).

[14]D. S. Gaunt and M. F. Sykes, to be published.

[15]V. A. Vyssotsky, S. B. Gordon, H. L. Frisch, and J. M. Hammersley, Phys. Rev. 123, 1566 (1961).

[16]A. Geiger, R. L. Blumberg, and H. E. Stanley, to be published.

[17]D. S. Gaunt, S. G. Whittington, and M. F. Sykes, J. Phys. A 14, L247 (1981), and references therein.

[18]A. G. Dunn, J. W. Essam, and D. S. Ritchie, J. Phys. C 8, 4219 (1975).

[19]M. A. A. Cox and J. W. Essam, J. Phys. C 9, 3985 (1976).

[20]D. Heermann and D. Stauffer, Z. Phys. B 44, 339 (1981).

[21]D. S. Gaunt, J. Phys. A 10, 807 (1977).

[22]A. Coniglio, H. E. Stanley, and D. Stauffer, J. Phys. A 12, L323 (1980).