

Model for gelation with explicit solvent effects: Structure and dynamics

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We study a two-component model for gelation consisting of f -functional monomers (the gel) and inert particles (the solvent). After equilibration as a simple liquid, the gel particles are gradually cross linked to each other until the desired number of cross links have been attained. At a critical cross-link density, the largest gel cluster percolates and an amorphous solid forms. This percolation process is different from ordinary lattice or continuum percolation of a single species in the sense that the critical exponents are new. As the cross-link density p approaches its critical value p_c , the shear viscosity diverges: $\eta(p) \sim (p_c - p)^{-s}$ with s a nonuniversal concentration-dependent exponent.

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I. INTRODUCTION

It is generally accepted that percolation is an essential aspect of gelation or vulcanization—it is doubtful that even in a highly entangled melt of long polymers, a nonzero value of the static shear modulus could exist in the absence of an infinite connected network. However, percolation has usually been studied in rather special limits. Site and bond percolation of a single species on regular lattices are very well characterized and off-lattice percolation seems to present no new features [1], at least insofar as critical behavior is concerned. More closely related to real gels are the so-called correlated percolation models where the distribution of cross links is drawn from a Boltzmann distribution appropriate for a nearest neighbor lattice gas [2]. Except at special points in the phase diagram, these models are also in the universality class of the simple percolation problem. In our previous work on transport properties near the gel point [3], we have also used a simple one-species percolation process to produce the incipient gel. We found that the shear viscosity diverges as the percolation concentration p_c is approached according to $\eta(p) \sim (p_c - p)^{-s}$ with $s \approx 0.7$. This value of the exponent s is in excellent agreement with a prediction of de Gennes based on a superconductor–normal conductor analogy [4] and with recent analytical work on a Rouse model [5]. It is also reasonably close to some experimental results for s [6] but quite different from that produced by another set of experiments $1.1 \leq s \leq 1.3$ [7]. Thus, it seems reasonable to ask if different versions of the cross-linking process might produce significantly different cluster size distributions from percolation and, consequently, different rheological properties.

Gelation often occurs in the presence of a solvent and over some period of time rather than instantaneously, as in the usual percolation models. To simulate this feature, we have considered a two-species model consisting of a fraction c of f -functional particles that are eligible to bond irreversibly to others of the same kind. The remaining particles are inert and function as a background liquid, through which the

gel particles and clusters diffuse. Cross linking occurs in stages: the equations of motion of all the particles are integrated forward for a fixed number of time steps between cross-linking attempts and this process is continued until the desired number of cross links is attained. At a critical concentration of cross links p_c (in the thermodynamic limit), the largest cluster percolates and an amorphous solid forms. For this process, one can calculate the usual static or geometrical quantities used to characterize percolating systems, e.g., the fraction of particles on the “infinite cluster” $P_\infty(p) \sim (p - p_c)^\beta$, the mean mass of finite clusters $S(p) \sim |p - p_c|^{-\gamma}$, the fraction of samples percolating $f(p)$, and the cluster size distribution $n(m, p) = m^{-\tau} \phi(m | p - p_c |^{1/\sigma})$, where m is the mass of a cluster and the radius of gyration $R_g(m) \sim m^{1/D}$, where D is the fractal dimension of the clusters. For simple percolation processes, $\tau \approx 2.18$, $\sigma \approx 0.45$, and these two exponents determine the others through scaling relations [1]. Here we find, at least for small c , that the cluster size distribution, even at p_c , is not well described by a simple power law. However, the other static quantities listed above do display power law behavior near p_c and a standard finite-size scaling analysis provides a very good collapse of our data. Moreover, the hyperscaling relation $2\beta + \gamma = d\nu$, where $d = 3$ is the dimensionality and ν the correlation length exponent, is satisfied. This suggests that this percolation transition is fundamentally describable in terms of a fixed point with two (at least) relevant scaling fields. As the percolation point is approached from below, the shear viscosity diverges according to $\eta(p) \sim (p_c - p)^{-s}$. In contrast to our previous work on a model without solvent, we find values of s in the range $0.3 \leq s(c) < 0.45$ as compared with $s \approx 0.7$. These results suggest that the critical behavior of transport coefficients of systems close to the gel point is nonuniversal.

The structure of this article is as follows. In Sec. II, we describe the present model and simulation procedures in more detail. The geometric properties of the system are discussed in Sec. III and the data on the shear viscosity are presented in Sec. IV. We conclude with a brief summary and discussion in Sec. V.

II. THE MODEL

We consider a system of N particles in three dimensions, all of which interact with each other through the soft-sphere potential $V(r_{ij}) = \epsilon(\sigma_0/r_{ij})^{36}$ for $r_{ij} < 1.5\sigma_0$ [8]. We simulated systems at a temperature $k_B T/\epsilon = 1$ and volume fraction $\Phi = \pi\sigma_0^3 N/6V = 0.4$, which is well below the liquid-solid coexistence density. In the absence of any other interactions, this system would be a simple three-dimensional liquid. We initially place the particles on a simple cubic lattice that fills the computational box. We then randomly select $N_{gel} = cN$ particles to be the gel forming component. After equilibration of the system with Brownian dynamics, with periodic boundary conditions, for 10 000 time steps, we begin the cross-linking process. At this point, the calculation proceeds via *conservative* molecular dynamics (MD) so as to allow hydrodynamic modes to develop. Here, we use a time step $\delta t = 0.005 \sqrt{m\sigma_0^2/\epsilon}$. In the smallest system, cross linking is carried out one bond at a time. A single gel particle is randomly selected and all other gel particles within a distance of $1.2\sigma_0$ are identified. One of the particles in this list is randomly selected and bonded irreversibly to the central particle through the tethering potential $V_{nn}(r_{ij}) = \frac{1}{2}k(r_{ij} - r_0)^2$, with $k = 5\epsilon/\sigma_0^2$ and $r_0 = (\pi/6\Phi)^{1/3}\sigma_0$. Each gel particle is allowed to bond to no more than six others and bonding between any pair of particles occurs at most once. The configuration of the entire system is then updated for 100 time steps and the entire bonding process is repeated until $3pN_{gel}$ cross links have been added [9]. The parameter p is analogous to the occupation probability in a bond percolation process on the simple cubic lattice. In larger systems, the number of cross links added in the bonding steps is scaled by the system size in order to keep the cross-linking rate per gel particle constant.

The parameters in the potentials and the total volume fraction Φ are the same as in our previous work [3]. The differences are that in this earlier work, all particles were considered to be gel particles and that the cross linking was done instantaneously, at $t = 0$, when the particles were on the vertices of a cubic lattice and thus all structural properties were those of percolation in three dimensions. The present model is similar in some ways to a model discussed by Gimel *et al.* [10] and Hasmy and Jullien [11] who studied percolation in the context of diffusion-limited cluster-cluster aggregation using Monte Carlo methods. Their model differs from ours in that it is a lattice model, in the details of the cross-linking process, in the lack of solvent, and in the nature of the cluster dynamics. In Monte Carlo simulations, one is forced to arbitrarily choose the mass-dependent diffusion constant $D(m)$ whereas in our molecular dynamics calculations, it is determined by the existing structure and the interparticle forces. In the regime that is of interest here, i.e., high enough gel density that percolation is possible, these authors find the critical behavior of ordinary percolation.

In a separate set of runs, we calculate the stress-stress autocorrelation function and, through the appropriate Green-Kubo formula, the shear viscosity. Equilibration and cross linking are carried out as described above and the calculation of the viscosity is again done with a conservative MD.

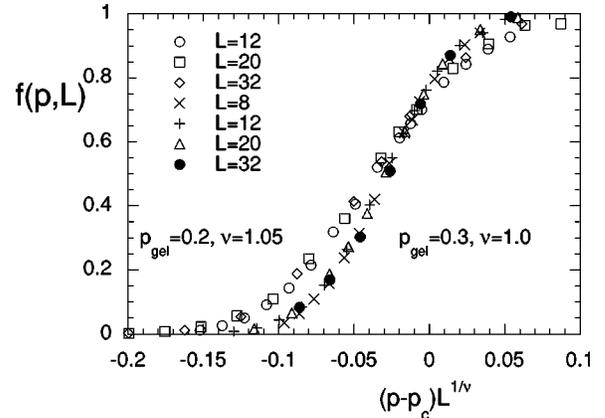


FIG. 1. Fraction of samples percolating for $c = 0.2$ and $c = 0.3$ as a function of the scaled cross-link concentration $x = (p - p_c)L^{1/\nu}$ for $8 \leq L \leq 32$. The values of the exponent ν used are 1.05 for $c = 0.2$ and 1.0 for $c = 0.3$. For $L = 8$, we have simulated 20 000 independent cross linkings at each p ; for $L = 32$ the data are derived from 3000 samples for each p . All quantities are dimensionless.

The adjustable parameters in our calculations are the gel fraction c , the cross-link density p , and the system size. Here, we report results for $c = 0.2, 0.3$, and 1.0 . Calculations for other values of c are in progress and will be reported in a future publication [12]. We parametrize the size of our system in terms of the dimensionless length $L = N^{1/3}$, where N is the total number of gel and solvent particles. Because the cross-linking process is itself quite time consuming, we are able only to simulate systems up to size $L = 32$ (32 768 particles) and this makes our estimates of critical exponents rather imprecise. A second factor contributing to the uncertainty in critical exponents is that we need to determine the critical cross-link density p_c for each value of c , whereas for lattice percolation, this number is known to a high accuracy. We next discuss the static (geometric) properties of our model.

III. PERCOLATION

The critical concentration p_c , at which percolation occurs in the thermodynamic limit $L \rightarrow \infty$ is accurately estimated from the intersection of curves $f(p, L)$ as a function of p for different values of L . Here $f(p, L)$ is the fraction of samples percolating in a system of size L at cross-link concentration p . For the two cases of interest here, $c = 0.3$ and $c = 0.2$, we find $p_c = 0.3165 \pm 0.0005$ and $p_c = 0.3735 \pm 0.001$. Once p_c has been determined, the correlation length exponent ν can be estimated from the collapse of the data for the function f when plotted as function of $(p - p_c)L^{1/\nu}$. We show this collapse of the data for $c = 0.2$ and 0.3 in Fig. 1. For $c = 0.3$, the best collapse of the data for $8 \leq L \leq 32$ is obtained for $\nu = 1.0$, which should be compared to the three-dimensional percolation result $\nu = 0.88$. For $c = 0.2$, finite-size effects are more pronounced and the data for $L = 8$ have been excluded. For this case, the best collapse of the data is obtained for $\nu = 1.05$. This method of estimating a critical exponent is not very accurate but the three-dimensional percolation value $\nu = 0.88$ provides a significantly worse collapse of the data.

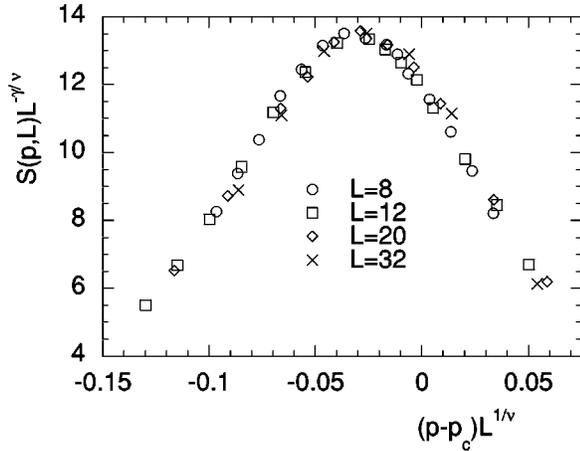


FIG. 2. Scaled form of the mean mass of finite clusters $L^{-\gamma/\nu}S(p,L)$ for $c=0.3$ and $8 \leq L \leq 32$. Here, $\gamma/\nu=1.815$ and $\nu=1.0$. Here, the mass of a cluster refers to the number of particles in the cluster.

We next discuss the mean size of finite clusters because this data provides an unbiased estimate of the ratio γ/ν . In the thermodynamic limit, $S(p) \sim |p-p_c|^{-\gamma}$ with $\gamma \approx 1.8$ for $d=3$ percolation. For finite L , $S(p,L)$ is peaked near p_c with a peak height that grows as $L^{\gamma/\nu}$. Therefore, rescaling the peak heights to the same value for different L provides an estimate of γ/ν that is not affected by errors in either p_c or ν . Of course, the overall collapse of the data to a universal curve depends on accurate determination of these two quantities but the peak height does not. In Figs. 2 and 3, we show the function $L^{-\gamma/\nu}S(p,L)$ plotted as a function of $x=(p-p_c)L^{1/\nu}$ for the previously determined values of p_c and ν . The collapse to a universal curve is quite respectable for both $c=0.3$ and 0.2 for $\gamma/\nu=1.815$ and 1.80 , respectively. As above, the data for $L=8$ have been excluded for $c=0.2$. We note that in the case of three-dimensional percolation, the ratio $\gamma/\nu \approx 2.05$. Use of this value of γ/ν in Fig. 2 would result in a 40% difference between the peak heights for $L=32$ and $L=8$.

In the scaling theory of percolation [1], the ratio γ/ν

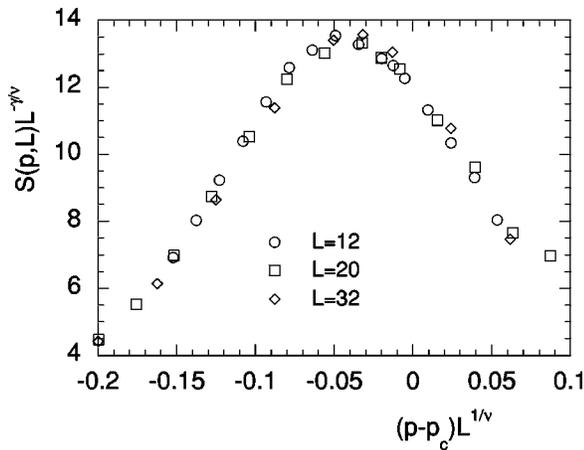


FIG. 3. Same as Fig. 2 in this case for $c=0.2$ with $\gamma/\nu=1.80$.

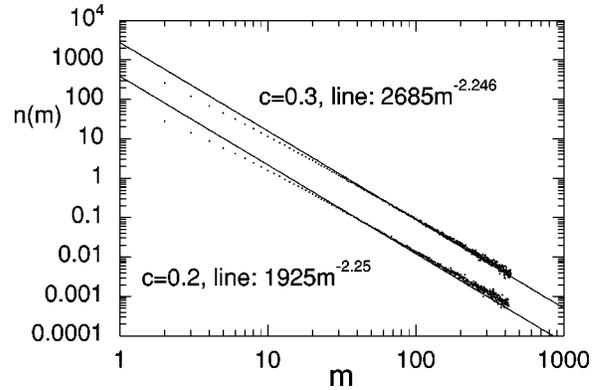


FIG. 4. Number of clusters $n(m)$ of mass m for $p \approx p_c$ for $c=0.2$ and 0.3 . The data for $c=0.2$ have been lowered by a factor of 5 for separation of curves. The straight lines represent fits to $am^{-\tau}$ with τ determined by imposing hyperscaling (see text). Both n and m are dimensionless.

$=d(3-\tau)/(\tau-1)$, where $d=3$ is the dimensionality and τ is the exponent characterizing the cluster size distribution at $p=p_c$. If we enforce this scaling relation, we obtain $\tau \approx 2.25$ for both $c=0.2$ and $c=0.3$. Using $\sigma=(\tau-1)/d\nu$, we find $\sigma(c=0.3)=0.415$ and $\sigma(c=0.2)=0.417$. Using $D=1/(\sigma\nu)$ for the fractal dimension results in the prediction $D(c=0.3)=2.41$ and $D(c=0.2)=2.29$ for the fractal dimensions of the clusters. As well, the hyperscaling relation $2\beta/\nu=3-\gamma/\nu$ yields $\beta/\nu=0.593$ and 0.6 for $c=0.3$ and 0.2 , respectively. The accuracy of these scaling predictions is tested in Figs. 4–7.

In Fig. 4, we show the number of clusters $n(m)$ of mass m at $p \approx p_c$ for $c=0.2$ and 0.3 for $L=32$ and $m \leq 400$. For the case $m=1$, we have only counted the uncross-linked gel particles. In neither case is the data well described by a simple power law, in contrast to percolation on a lattice or in the absence of solvent, where the exponent $\tau \approx 2.18$ is already obtained for $2 \leq m \leq 20$. A fit to a power law over the range $20 \leq m \leq 400$ yields $\tau=2.13$ for $c=0.2$ and $\tau=2.16$ for $c=0.3$. The straight lines in Fig. 4 are the best fits to the

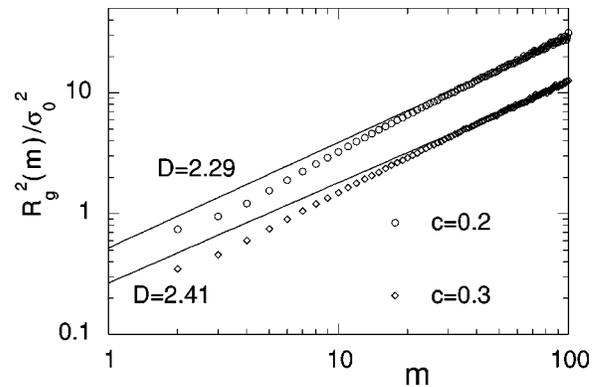


FIG. 5. Square of the radius of gyration $R_g^2(m)$ divided by the square of the hard core diameter, σ_0^2 , as a function of cluster mass m for $p \approx p_c$ and $c=0.2$ and 0.3 . Straight lines are fits to $R_g^2(m) = am^{2D}$ with the fractal dimensions determined by requiring that hyperscaling hold (see text).

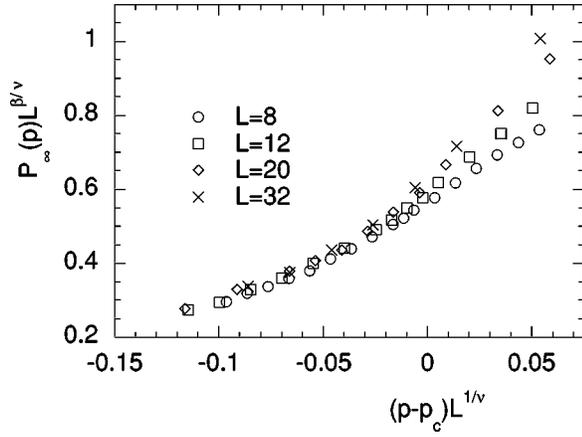


FIG. 6. Plot of the scaled form of the order parameter $P(L,p)$ for $p_g=0.3$ and $8 \leq L \leq 32$. The exponents are $\beta/\nu=0.593$ and $\nu=1.0$. All quantities are dimensionless.

form $n=Am^{-2.25}$ over the range $20 \leq m \leq 400$ and while the fit is not perfect, the data are not inconsistent with this behavior in the limit of large m .

In Fig. 5, we show the square of the radius of gyration $R_g^2(m)$ as a function of m for a system of size $L=32$, together with curves $m^{2/D(c)}$ with $D(c=0.2)=2.29$ and $D(c=0.3)=2.41$ as determined above. The data again show considerable curvature but the fit to the assumed functional form is reasonable over the range $20 \leq m \leq 100$.

Finally, in Figs. 6 and 7, we display the scaled form of $P(L,p)$, the probability that a gel particle is a part of the percolating cluster using the predicted exponent ratios $\beta/\nu=0.593$ for $c=0.3$ and $\beta/\nu=0.6$ for $c=0.2$. These two figures present the least impressive collapse of data to a universal curve, especially at the larger values of P . One can improve the collapse by different choice of β/ν and ν but at the expense of violating hyperscaling. We also note that the data for the two largest values of L are reasonably close to each other over the entire range of x .

We have also carried out a limited number of simulations for $c=0.5$ and $c=1.0$ with the cross-linking process described above. In both cases, the critical exponents and the

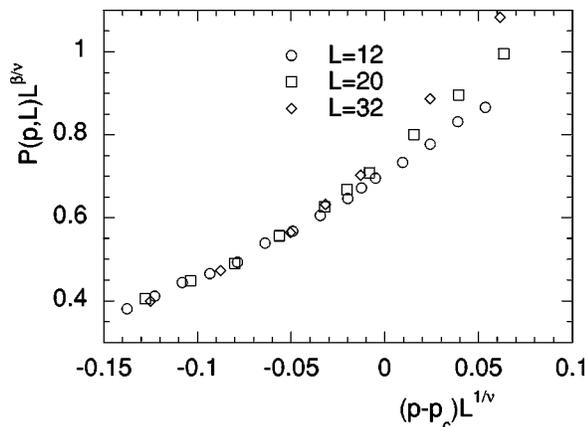


FIG. 7. Same as Fig. 6 but for $c=0.2$ and $\beta/\nu=0.6$ and $\nu=1.05$.

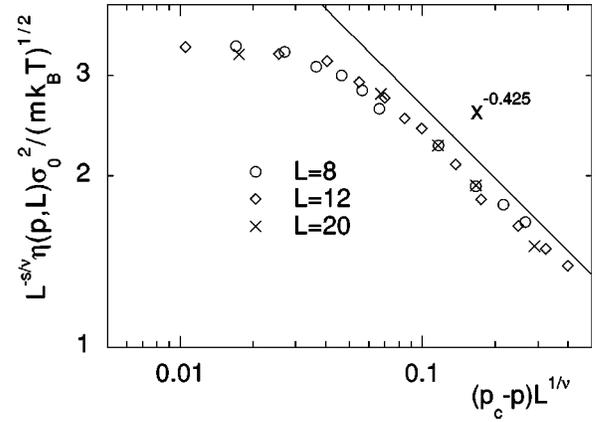


FIG. 8. The dimensionless shear viscosity $\sigma_0^2 \eta(L,p)/(mk_B T)^{1/2}$ for $c=0.3$ times $L^{-s/\nu}$ plotted as a function of $x=(p-p_c)L^{1/\nu}$ with $s/\nu=0.425$ and $\nu=1.0$. The straight line represents the function $x^{-s/\nu}$ (see text).

cluster size distributions are entirely consistent with ordinary three-dimensional percolation. This suggests that either there is a critical gel fraction [13], below which the geometric properties of the clusters are described by continuously varying exponents or that the apparent variation of the exponents with c described above is a finite-size artifact. Only simulations of larger systems can resolve this issue.

IV. SHEAR VISCOSITY

We have calculated the shear viscosity for systems up to size $L=20$ as a function of the cross-link density p for $c=0.3$ and for $L=12$ for $c=0.2$. Systems are equilibrated as a liquid, cross linked as described above and then evolved by constant energy MD for 40 000 or 80 000 time steps, depending on the cross-link density. Here, we have typically used 500–2000 different realizations of the cross links at each p . We calculate, as in Ref. [3], the stress-stress autocorrelation function $C_{\sigma\sigma(t)} = \frac{1}{3} \sum_{\alpha < \beta} \langle \sigma_{\alpha\beta}(t) \sigma_{\alpha\beta}(0) \rangle$, where

$$\sigma_{\alpha\beta} = \sum_{i=1}^N m v_{i\alpha} v_{i\beta} - \sum_{i < j} \frac{r_{ij\alpha} r_{ij\beta}}{r_{ij}} V'(r_{ij})$$

are elements of the stress tensor. Here, the sum is over both gel and solvent particles and V' is the derivative of the pair potential between particles i and j . The analysis of the stress-stress correlation function has been described in Ref. [3] and is done in the same way here. As $p \rightarrow p_c$, $C_{\sigma\sigma}$ decays extremely slowly and is fitted, at long times, to a stretched exponential. The static shear viscosity is then obtained from the appropriate Green-Kubo formula [14],

$$\eta = \lim_{t_{max} \rightarrow \infty} \frac{1}{V k_B T} \int_0^{t_{max}} C_{\sigma\sigma}(t) dt.$$

The results for $c=0.3$ are shown in finite-size scaled form in Fig. 8, where $L^{-s/\nu} \eta(L,p)$ is plotted as a function of the scaled concentration x [15]. In contrast to our previous result for $c=1$ and instantaneous cross linking where we found s

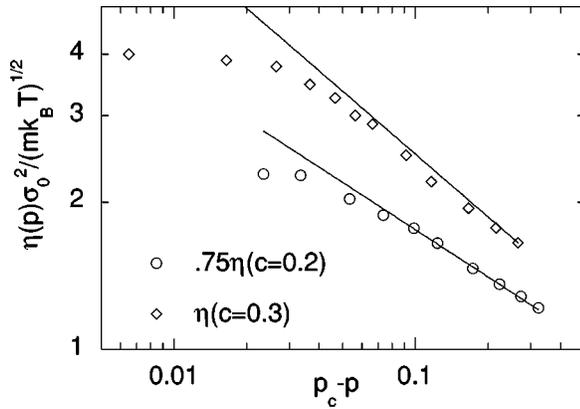


FIG. 9. The dimensionless shear viscosity $\sigma_0^2 \eta(p)/(mk_B T)^{1/2}$ for $L=12$ and $c=0.2$ and 0.3 plotted as a function of $(p_c - p)$. The straight line represents the function $(p_c - p)^{-s}$ with $s=0.425$ for $c=0.3$ and $s=0.3$ for $c=0.2$.

≈ 0.7 , we find that $s \approx 0.425$ provides an excellent collapse of the data with $\nu=1.0$. We note that, outside the critical region, consistency of the finite-size scaling ansatz requires the scaled viscosity to vary as $x^{-s/\nu} = x^{-0.425}$ and it is clear that the data are consistent with this behavior.

We have also calculated the shear viscosity for $c=0.2$ for $L=12$. The raw data are displayed in Fig. 9 as a function of $p_c - p$, together with the corresponding results for $c=0.3$. Fitting to a power law outside the critical region produces an exponent $s \approx 0.3$ suggesting, as in the case of the static properties, a variation of critical exponents with c and an absence of universality.

V. DISCUSSION

In this article, we have proposed and investigated a different model for gelation which incorporates a solvent on a microscopic level. For relatively small concentrations of gel, the geometric properties of the system close to the gel point seem to depend continuously on this gel fraction and are, at least for the system sizes investigated, markedly different

from three-dimensional percolation. In particular, the fractal dimension of the clusters seems to be smaller than those of percolation clusters and this more spidery morphology may be responsible for the slower divergence of the shear viscosity as the gel point is approached. The change in the exponents controlling the geometric properties is rather small and further study of larger systems is certainly necessary to confirm this result. However, the exponent s that characterizes the divergence of the shear viscosity at the gel point is reduced by almost a factor of 2 from its value in the absence of solvent and it is unlikely that this can be attributed to finite-size effects. In light of this result, it seems implausible that a single universality class describes the behavior of transport coefficients and, presumably, the moduli of the amorphous phase near the gel point. The considerable dispersion found in experimental values of the critical exponents [16] is another indicator that this may be the case.

In future work, we intend to explore this different model in greater detail. It will be interesting to investigate if the exponent s and the static exponents are tunable by varying the concentration of the solvent and the solubility of the solute. We also intend to study diffusion constants as a function of cluster size and to investigate the existence of long time tails. Finally, one of the original motivations for this model is the existence of a body of experimental work that has yielded values in the range 1.1–1.3 for the viscosity exponent s . Clearly, we have moved further from this range of values compared to our previous results. If the cluster size distribution and cluster geometry is the determining factor in the critical behavior of the transport coefficients then this indicates that models that produce more compact rather than more tenuous clusters than those arising from percolation may be appropriate.

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- similar to the site-bond percolation process [1]. In future work, we expect to investigate the effects of different time delays on the scaling properties at the percolation point.
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