

Viscoelasticity near the gel point: A molecular dynamics study

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We report on extensive molecular dynamics simulations on systems of soft spheres of functionality f , i.e., particles that are capable of bonding irreversibly with a maximum of f other particles. These bonds are randomly distributed throughout the system and imposed with probability p . At a critical concentration of bonds, $p_c \approx 0.2488$ for $f=6$, a gel is formed and the shear viscosity η diverges according to $\eta \sim (p_c - p)^{-s}$. We find $s \approx 0.7$ in agreement with some experiments and with a recent theoretical prediction based on Rouse dynamics of phantom chains. The diffusion constant decreases as the gel point is approached but does not display a well-defined power law.

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I. INTRODUCTION

The behavior of transport coefficients and elastic moduli near the gelation transition has been discussed in the literature for many years [1]. To date no consensus on either the theoretical or experimental side has emerged as far as the critical behavior of these quantities is concerned. The phenomenology is as follows. As monomers or polymers are randomly cross-linked to each other in a melt, the shear viscosity η increases with cross-link concentration p and diverges at a critical concentration p_c at which an amorphous rigid network is formed. Experiment and theory both yield $\eta \sim (p_c - p)^{-s}$ but there is no general agreement regarding the value of the exponent s . One group of experiments has produced exponent values for the shear viscosity in the range $0.6 \leq s \leq 0.9$ [2,3]. Another group [4–6] has reported values for s in the range 1.1–1.3 and used a scaling ansatz to interpret these results [4]. At this point it is not clear if these quite different values of the exponent result from different physical mechanisms or if experimental problems are responsible. The experimental situation is complicated by the fact that the size of the basic units can affect the size of the critical region: As de Gennes showed [7], vulcanization (cross-linking of very long chains) must be distinguished from gelation (cross-linking of short chains or monomers). As the chain length increases, the critical region becomes smaller and the behavior remains mean field like over a larger range of p . This conclusion is supported by recent experiments [4,8] which show quite clearly that chain length is a relevant parameter.

There is also considerable disagreement as far as theory is concerned. Many years ago, de Gennes [9] argued that the viscosity is analogous to the conductivity of a random mixture of normal conductors and superconductors, with an exponent $s \approx 0.67$. The scaling argument mentioned above [4] predicts $s = 2\nu - \beta \approx 1.35$, where $\nu \approx 0.88$ and $\beta \approx 0.41$ are the correlation length and order parameter exponents of percolation theory in three dimensions. Finally, a recent theoretical analysis of randomly cross-linked phantom (i.e., non-self-avoiding) polymers with Rouse dynamics [10] yields s

$= \phi - \beta \approx 0.7$ where $\phi \approx 1.11$ is the crossover exponent of a random resistor network. Given this wide disparity in both theoretical and experimental results, computer simulations may help to clarify the situation.

Dynamical scaling theory relates the viscosity below the gel point and the modulus above the gel point [1]. The shear modulus μ of a rigid network near the gel point is typically entropic in nature and vanishes with a power law of its own as the gel point is approached from the rigid phase: $\mu \sim (p - p_c)^t$. Recent numerical work on systems in the percolation universality class [11] has provided evidence that the exponent t is the same as that of the conductivity of a randomly disordered network of conductors and insulators near the percolation point. This result is consistent with another argument of de Gennes [12]. In the dynamical scaling theory of the gelation transition, the two exponents t and s are not independent, but rather obey the sum rule $s + t = z$ where z describes the divergence of the longest relaxation time in the incipient gel: $t^* = t_0(p_c - p)^{-z}$ [1]. Moreover, at high frequencies the complex viscosity $\eta^*(\omega) \equiv \eta'(\omega) + i\eta''(\omega)$ is expected to decrease according to $\eta', \eta'' \sim \omega^{u-1}$ with $u = t/s + t$ and with $\eta'/\eta'' = \tan \pi u/2$. This connection allows an important consistency check between the results reported here and those of [11].

The structure of this article is as follows. In Sec. II we describe our model and computational methods. Section III contains the bulk of the results. We conclude in Sec. IV with a discussion and outlook for future work.

II. MODEL AND COMPUTATIONAL METHODS

The model that we simulate is capable of describing the entire range from simple liquid to entropic solid. We consider a system of soft spheres in three dimensions. All particles interact through the potential $V_{sa}(r_{ij}) = \epsilon(\sigma/r_{ij})^{36}$ for $r_{ij} \leq 1.5\sigma$ [13] with $\sigma = 1$ and, for our simulations, $k_B T/\epsilon = 1$. If there are no other interactions, this system forms a simple three-dimensional liquid at least at low density. All of our simulations are done at a volume fraction $\Phi = \pi N \sigma^3 / 6V = 0.4$ which is well below the liquid-solid coex-

istence density. The viscosity of the system is progressively increased by introducing random cross-links between particles. In order to ensure that the gel point coincides with the geometrical percolation point, we choose a very special initial condition. Specifically, the system of particles is initially placed on a simple cubic lattice that fills the cubic computational box. Each particle may bond with probability p with each of its six nearest neighbors. This step is precisely the same as a bond-percolation process on the simple cubic lattice. The bonding is permanent and enforced by the spherically symmetric potential $V_{nn}(r_{ij}) = \frac{1}{2}k(r_{ij} - r_0)^2$ with $k = 5\epsilon/\sigma^2$ and $r_0 = (\pi/6\Phi)^{1/3}\sigma$. This choice of r_0 ensures that the system is unstrained for all p , at least at $T=0$. The advantage of this cross-linking procedure is that we have a very accurate estimate of the percolation probability $p_c \approx 0.2488$ [14] and thus one less source of potential error. On the other hand, it is certainly conceivable that the dynamics in the sol phase can influence the topology and connectivity of the incipient gel. The present model does not incorporate such effects. We shall return to this point in Sec. IV.

For $p < p_c$, the system consists of finite clusters of varying masses. For $p > p_c$ the system is an entropic solid with nonvanishing shear modulus. This system has been previously studied by us [11] for $V_{sa}=0$ and $p > p_c$. As mentioned above, the results in both two and three dimensions indicate that the moduli of such “phantom networks” are controlled by the same exponent as the conductivity of a random resistor network. More recently, Farago and Kantor as well as Cohen and Plischke [15] have shown that self-avoidance is irrelevant as far as the critical behavior of the elastic constants is concerned.

Once the cross-links or bonds have been imposed, the particles move in the full three-dimensional space, subject to periodic boundary conditions. The system of particles is first equilibrated for 5×10^4 time steps with Brownian dynamics. At the end of this equilibration time, the damping and thermal noise are turned off and the subsequent evolution is conservative. The equations of motion are integrated with a standard velocity Verlet algorithm [16] with a time step of $\delta t = 0.005\sqrt{m\sigma^2/\epsilon}$. The shear viscosity $\eta(p)$ and the self-diffusion constant $D(p)$ are then calculated from the appropriate Green-Kubo formula [17]:

$$\begin{aligned} \eta &= \lim_{t_{max} \rightarrow \infty} \int_0^{t_{max}} dt C_{\sigma\sigma}(t) \\ &= \lim_{t_{max} \rightarrow \infty} \frac{1}{3Vk_B T} \int_0^{t_{max}} dt \sum_{\alpha < \beta} \langle \sigma^{\alpha\beta}(t) \sigma^{\alpha\beta}(0) \rangle, \end{aligned} \quad (1)$$

where

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

and where V' is the derivative of the total potential energy. Similarly, the diffusion constant is given by the familiar expression

$$D = \lim_{t_{max} \rightarrow \infty} \frac{1}{3N} \sum_{i=1}^N \int_0^{t_{max}} dt \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle. \quad (2)$$

It is well known that the velocity-velocity autocorrelation function decays extremely slowly, typically with a “long time tail” $t^{-3/2}$ power law, even in simple liquids [17]. We find the same long-time behavior in our simulations as well, remarkably for all values of p . There is considerably more disagreement regarding the stress-stress correlation function. Extended mode-coupling theory [18] suggests that close to the melting point the stress correlator decays exponentially at long times. Powles and Heyes [13] have found that both an exponential decay and a Lorentzian provide a reasonably good fit to their data in the dense liquid regime. More recently, Broderix *et al.* [19] have shown, using Rouse dynamics for a system of Gaussian polymers with randomly positioned cross-links, that the stress correlator decays according to a stretched exponential form $C_{\sigma\sigma} \sim \exp\{-(t/\tau)^\lambda\}$ with a nonuniversal exponent λ ($0.2 < \lambda < 0.5$) throughout the sol phase. We have also found that the stretched exponential function provides a very good fit to the data close to the gel point, typically with an exponent $\lambda \approx 0.2$. In any case, the decay of $C_{\sigma\sigma}$ is dramatically affected by cross-linking and becomes very slow close to the gel point. Therefore in the evaluation of Eqs. (1) and (2) we have used time series from $t_{max} = 300\tau$ to $t_{max} = 1200\tau$ where τ is the average time between collisions for particles in the non-cross-linked liquid ($p=0$). Even with such long runs, for p close to p_c an estimate of the residual integral to $t = \infty$ had to be added. This is discussed further below.

III. RESULTS

We have simulated systems consisting of $N=L^3$ particles with $L=5, 8, 12$, and 20 , the first three over the concentration range $0 \leq p \leq 0.24$, the fourth only for $p \geq 0.20$. For these relatively small systems, the probability that one of the clusters percolates in at least one of the three directions is an issue. If there is percolation, then the viscosity is not a well-defined quantity and the sample is characterized instead by a shear modulus. Therefore, we have eliminated all percolating samples from the calculation. For $L=5$, a non-negligible number of samples percolates in at least one direction already at $p=0.15$; at $L=20$ percolation becomes significant only at $p=0.23$.

Figure 1 depicts the stress correlator for $N=12^3$ particles for several cross-link concentrations. The top panel shows this function over the entire range in time, the lower panel for $t > 2\tau$. The top panel shows that $C_{\sigma\sigma}(t)$ is essentially unaffected by cross-linking for small t . The effect of increasing cross-link density is illustrated in the lower panel, where it is clearly seen that the decay of the correlation function becomes progressively slower as the gel point is approached and that even at $t=1200\tau$, for $p \geq 0.2$, the correlator is non-negligible. Therefore, integrating $C_{\sigma\sigma}(t)$ only to t_{max} would result in an underestimate of the shear viscosity. In order to capture the remaining contribution, we have fitted $C_{\sigma\sigma}(t)$ with a stretched exponential over various windows (t_s, t_{max}) for starting values $t_s > 2\tau$. Such a fit is shown in Fig. 1(b) for the uppermost curve ($p=0.24$) over the range $2\tau \leq t \leq t_{max}$. The fit is essentially indistinguishable from the

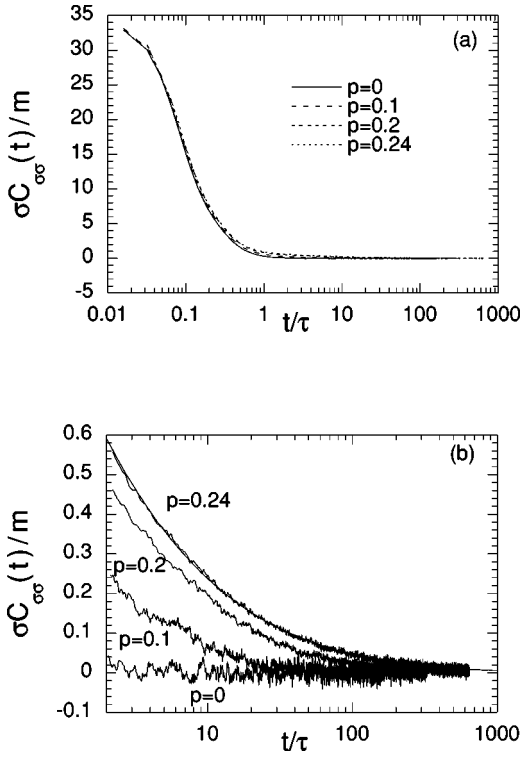


FIG. 1. The dimensionless stress-stress correlation function $\sigma C_{\sigma\sigma}/m$ for $L=12$ and several cross-linking probabilities for (a) all $t/\tau > 0$ and (b) $t/\tau > 2$. In the uppermost curve in (b) we also show the fit of $C_{\sigma\sigma}$ to a stretched exponential (solid line). For $p=0.1$ the data are obtained from 30 different cross-linkings; for larger p from between 100 and 200 cross-linkings.

simulation. As mentioned above, there is reason to believe [19] that the stretched exponential is the appropriate functional form at long times [20]. To check the quality of this fit and to obtain an estimate of the error in the shear viscosity due to this procedure, we have chosen several different starting points for the fit: the spread in values of the remaining integral of the fitting function from t_{max} to infinity provides an estimate of the error associated with this part of the calculation. For $p < 0.2$, the error due to the integration is negligible; for $p > 0.2$ we believe it to be less than 5%.

In Fig. 2 we display our data for the dimensionless shear modulus $\eta\sigma^2/\sqrt{mk_B T}$ in two versions. In part (a) the raw data are shown as a function of $(p_c - p)$ together with a guide to the eye of the form $a(p_c - p)^{0.7}$. This function clearly captures the general behavior of the data in the intermediate range of p . For p close to zero, one would not expect the system to anticipate the formation of a gel at $p \approx 0.25$, and for p close to p_c finite-size effects are clearly evident. Part (b) of this figure attempts to collapse the data by means of the finite-size scaling ansatz $\eta(L, p) = L^{s/\nu} \Psi[L(p - p_c)^\nu]$ [21] with $s=0.7$ and $\nu=0.88$. Internal consistency requires that the scaling function have the asymptotic form $\Psi(x) \sim x^{-s/\nu}$ for large x and a line corresponding to this form is also shown on the figure.

Further support for the conclusion $s \approx 0.7$ comes from the complex frequency-dependent viscosity $\eta^*(\omega) \equiv \eta'(\omega) + i\eta''(\omega) = G^*(\omega)/(i\omega)$ where G^* is the complex elastic

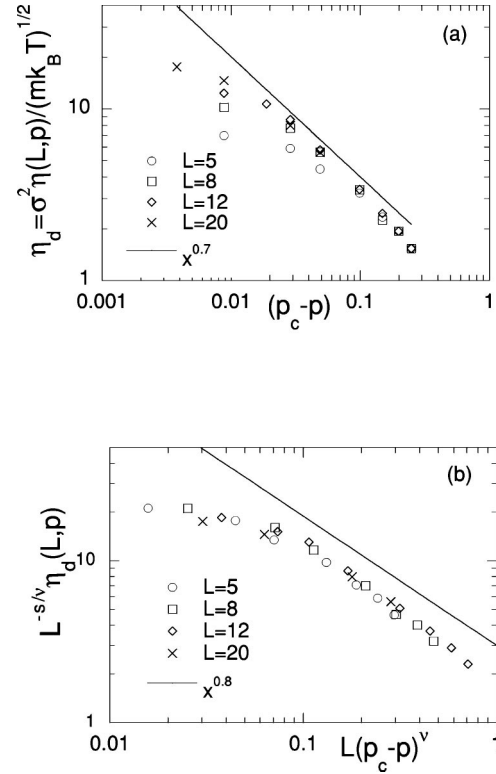


FIG. 2. Log-log plot of the dimensionless shear viscosity as a function of cross-linking probability p : (a) raw data; (b) finite-size scaling form of the data.

modulus. The scaling ansatz for these functions [1] is $\lim_{\omega \rightarrow 0} \eta'(\omega) \sim (p_c - p)^{-s}$ for $p < p_c$; $\lim_{\omega \rightarrow 0} G'(\omega) \sim (p - p_c)^t$ for $p > p_c$; and, for frequencies $\omega > \omega^*$, where ω^* is a characteristic crossover frequency that approaches zero as $p \rightarrow p_c$, $G^*(\omega) \sim (i\omega)^u$. The connection between the critical behavior of the modulus in the rigid phase and the viscosity in the fluid phase is then expressed through the scaling relation $u = t/(s+t)$. Moreover, in the high frequency region, one expects $\eta'(\omega)$ and $\eta''(\omega)$ to both vary as ω^{u-1} and the ratio of the real and imaginary parts to obey $u = 2/\pi \tan^{-1}\{\eta'/\eta''\}$. In our previous work on the rigid phase

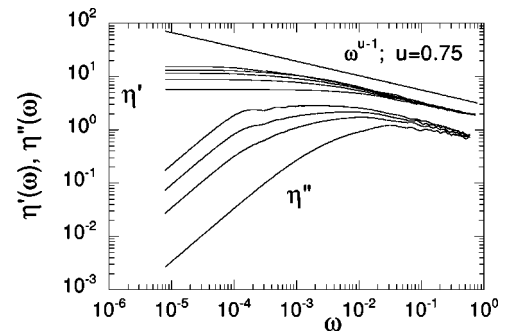


FIG. 3. Plot of the complex viscosity $\eta^*(\omega)$ as function of ω for $L=12$ and $p=0.2$ (lowest curve in each set), 0.22, 0.23, and 0.24 (top curve in each set). The power-law form $\eta \sim \omega^{u-1}$ is more evident for η' than for η'' and becomes more prominent as $p \rightarrow p_c$.

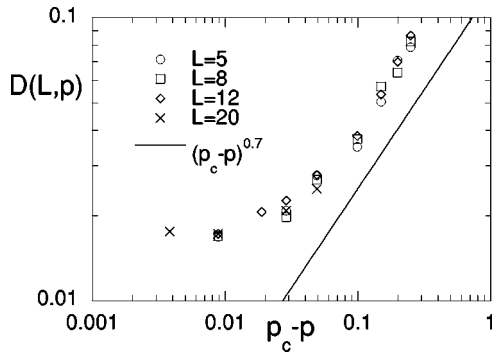


FIG. 4. The dimensionless diffusion constant $D(L,p)$ as a function of p . The straight line corresponds to a power law $(p_c - p)^{0.7}$.

[11], we concluded that $t \approx 2$ in three dimensions. Therefore, with $s \approx 0.7$ we have $u \approx 0.74$. The frequency-dependent viscosity is plotted in Fig. 3 for $L=12$ and $p > 0.20$. There is clearly a region of power-law behavior that extends to lower frequencies as the critical point is approached. This behavior is seen more clearly in η' than in η'' . Nevertheless, both pieces of the shear viscosity decrease in a way consistent with $\omega^{-0.25}$ in very satisfactory agreement with the foregoing discussion. The ratio of η' to η'' in this regime also produces a second estimate $u \approx 0.76$.

Finally, in Fig. 4 we show the dimensionless self-diffusion constant $\sqrt{m/\sigma^2 k_B T D}$ obtained from the velocity-velocity correlator (2) for *all* particles in the system. In this case, we show only the raw data. It seems clear from the behavior of D in the critical region that a finite-size scaling analysis is unlikely to improve the collapse of the data. For $p < 0.2$ the data are not inconsistent with a power-law behavior of the form $(p_c - p)^{0.7}$ but the evidence for this is weak at best. Moreover, the fact that the data for $p \approx p_c$ are essentially independent of L suggests that $D(L \rightarrow \infty, p \rightarrow p_c)$ is finite. Precisely at the gel point, in the thermodynamic limit, the system consists of a percolating cluster with fractal dimension $D_F \approx 2.5$. The particles that are not on the spanning network are organized into finite clusters of various sizes. Approximately 18% remain as monomers that presumably are able to diffuse quite easily through the percolating cluster since this cluster contains holes on all length scales. This would account for the absence of critical behavior in D .

IV. DISCUSSION

The results presented above and those obtained previously [11,15] are consistent with the following physical picture of networks and viscoelastic materials for which percolation is the structural agent that generates the gel or network. The elastic constants decrease to zero at the percolation point with a power law that, within error bars, is the same as that

for the conductivity of a random resistor network. Also the viscosity in the gel phase diverges as the critical point is approached from below with an exponent, again within error bars, the same as that for the conductivity of a network of perfect conductors and resistors. Moreover, the complex frequency-dependent viscosity at high frequencies connects these two regimes and again the results support these conclusions. Finally, the results of the present paper are in agreement with recent theoretical work [10] on cross-linked phantom polymers subject to Rouse dynamics.

The relation of these calculations to experiment is less clear. While there have been some experiments [2,3] that have obtained an exponent s relatively close to ours, there is another set of results rather different [5,6,4], with s more than 50% higher than ours. The results of Lusignan *et al.* [4] are particularly interesting in that the system, consisting of very small units, has a cluster-size distribution that is well described by percolation theory. Therefore, one would expect our models to be applicable to this system, certainly as far as the static properties are concerned. However, the experimental system has rheological properties ($s \approx 1.36, t \approx 2.7$) very different from ours. At present we have no explanation for these differences. One possibility is that the slow gelation process in the experiment allows molecular diffusion to affect the structural properties much more than our “flash bonding” process does. This could change the connectivity of the units without necessarily affecting the size distribution of the clusters in a dramatic way. Such effects are easily incorporated in our models and will be the subject matter for future work.

We are aware of one previous simulation that attempted to address the critical behavior of the shear viscosity near the gel point. Recently del Gado *et al.* [22] simulated a very different model, namely, particles confined to the sites of a lattice and randomly cross-linked to form clusters of various sizes. This system was then evolved by a bond-fluctuation method and the diffusion constants D_m of clusters of mass m measured. They postulated the relation $D(R) \sim R^{-(1+s/\nu)}$, where R is the radius of gyration of a cluster, and from this determined $s \approx 1.3$. We are not aware of any rigorous derivation of this connection between diffusion and viscosity. However, it may be that their model simply contains different physics.

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