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 $\eta$ 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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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 crosslinked to each other in a melt, the shear viscosity $\eta$ increases with crosslink 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 $s$. Indeed there is good reason to expect at least two different universality classes: As de Gennes showed [3], vulcanization (crosslinking of very long chains) must be distinguished from gelation (crosslinking of short chains or monomers) as far as critical behavior is concerned. This conclusion is supported by recent experiments [1], which show quite clearly that chain length is a relevant parameter.

Before describing our model and calculations, we discuss briefly the experimental and theoretical situation for gels putatively in the percolation (short chains) universality class. One group of experiments has produced exponent values for the shear viscosity in the range $0.6 \leq s \leq 0.9$ [4]. Another group [4,6,17] has reported values for $s$ in the range $1.1 - 1.3$ and interpreted these in terms of a Rouse model without hydrodynamics. On the theory side, de Gennes [6] 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 aforementioned Rouse model prediction is $s = 2\nu - \beta \approx 1.35$, 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 a different model with Rouse-dynamics [10] has predicted $s = \phi - \beta \approx 0.7$ 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.

The shear modulus $\mu$ of a rigid network near the gel point is typically entropic in nature and it vanishes with a power law of its own as the gel point is approached from the rigid phase $\mu \sim (p_c - p)^t$. Recent numerical work on systems in the percolation universality class [1] has provided evidence that $t = f$ in both two and three dimensions, where $f$ is the exponent that describes the critical behavior of a randomly disordered network of conductors and insulators near the percolation point. This result is consistent with another argument of de Gennes [2]. 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]. This connection allows an important consistency check between the results reported here and those of [1].

The model that we simulate is capable of describing the entire range from simple liquid to entropic solid. All particles interact through a soft sphere potential $V_{\text{nn}}(r_{ij}) = \epsilon (\sigma/r_{ij})^{12}$ 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 away from the liquid-solid coexistence density. The viscosity of the system is progressively increased by introducing random crosslinks between particles. 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 bonding is permanent and enforced by the spherically symmetric potential $V_{\text{nn}}(r_{ij}) = \frac{1}{2} k (r_{ij} - r_0)^2$ with $k = 5\epsilon/\sigma^2$ and $r_0 = (\pi/6 \Phi)^{1/3} \sigma$. For $p < p_c$, where $p_c \approx 0.2488$ is the bond percolation probability of the simple cubic lattice, 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 \([1]\) for \( V_m = 0 \) and \( p > p_c \). Farago and Kantor and Cohen and Plischke \([11]\) have shown that self-avoidance is irrelevant as far as the critical behavior of the elastic constants is concerned.

In the simulations, the system of particles is first equilibrated for \( 5 \times 10^4 \) 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 \([15]\) with a time step of \( \delta t = 0.005 \sqrt{m_0 \sigma^2 / \tau} \). The shear viscosity \( \eta(p) \) and the self-diffusion constant \( D(p) \) are then calculated from the appropriate Green-Kubo formula \([10]\):

\[
\eta = \lim_{t_{\text{max}} \to \infty} \int_0^{t_{\text{max}}} dt C_{\sigma\sigma}(t)
\]

\[
= \lim_{t_{\text{max}} \to \infty} \frac{1}{3N k_B T} \int_0^{t_{\text{max}}} dt \sum_{\alpha < \beta} \langle \sigma^\alpha(t) \sigma^\beta(0) \rangle
\]

where

\[
\sigma^{\alpha\beta} = \sum_{i=1}^N m v_i \epsilon_{i\beta}^\alpha - \sum_{i<j} \frac{r_{ij}^\alpha r_{ij}^\beta}{r_{ij}} V'(r_{ij})
\]

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

\[
D = \lim_{t_{\text{max}} \to \infty} \frac{1}{3N} \sum_{i=1}^N \int_0^{t_{\text{max}}} dt \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle.
\]

It is well known that the velocity-velocity correlation function decays extremely slowly, typically with a ‘long time tail’ \( t^{-3/2} \) power law, even in simple liquids \([16]\). 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 \([17]\) 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. In our situation where clusters of various sizes form the system, the decay is dramatically affected by crosslinking and becomes very slow close to the gel-point. Therefore in the evaluation of \([12]\) we have used time series from \( t_{\text{max}} = 300\tau \) to \( t_{\text{max}} = 1200\tau \) where \( \tau \) is the average time between collisions for particles in the uncrosslinked 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.

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 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 a set of crosslink 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 the changes for short times between the liquid \( (p = 0) \) and the incipient gel \( (p = 0.24) \) are extremely small. The effect of increasing crosslink 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 the longest time, for \( p \geq 0.2 \) the correlator is nonnegligible. Therefore, integrating \( C_{\sigma\sigma}(t) \) only to \( t_{\text{max}} \) would result in an underestimate of the shear viscosity. In order to capture the remaining contribution, we have fit \( C_{\sigma\sigma}(t) \) with
a stretched exponential over various windows \((t_s, t_{\text{max}})\) for starting values \(t_s > 2\tau\). Such a fit is shown in Figure 2b for the uppermost curve \((p = 0.24)\) over the range \(2\tau \leq t \leq t_{\text{max}}\). The fit is essentially indistinguishable from the simulation. However, there is no fundamental reason to believe that a stretched exponential is the functional form of the long-time behavior of \(C_{\omega_s}(t)\). This is the reason why we have chosen several different starting points for the fit: the spread in values of the remaining integral of the fitting function from \(t_{\text{max}}\) to infinity provides an estimate of the error associated with this part of the calculation.

In Figure 2 we display our data for the dimensionless shear modulus \(\eta \sigma^2 / \sqrt{m k_B T}\) in two versions. In part (a) the raw data is shown as 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 \(\eta(L, p) = L^{\nu s / \omega} \Psi[L(p - p_c) \omega]^{s / \nu}\) with \(s = 0.7\) and \(\nu = 0.876\). 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.

![Figure 2](image-url)

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

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 modulus. The scaling ansatz for these functions is \(\lim_{\omega \to 0} \eta^* (\omega) \sim \left( p_c - p \right)^{-s}\) for \(p < p_c\); \(\lim_{\omega \to 0} G^* (\omega) \sim \left( p - p_c \right)^{\nu}\) for \(p > p_c\) and, for frequencies \(\omega \gg \omega^*\), \(\omega^*\) is a characteristic crossover frequency that approaches zero as \(p \to p_c, G^* (\omega) \sim (i \omega)^{\nu}\). 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 \(u = \tau/(s + t)\). Moreover, in the high frequency region, one expects \(\eta' (\omega)\) and \(\eta'' (\omega)\) to both vary as \(\omega^{u - 1}\) 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 [11], we have 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 \(\eta'\) than in \(\eta''\). Nevertheless, both pieces of the shear viscosity decrease in a way consistent with \(\omega^{-0.27}\) in very satisfactory agreement with the foregoing analysis. As well, the ratio of \(\eta'\) to \(\eta''\) in this regime produces a second estimate \(u \approx 0.76\).

![Figure 3](image-url)

**FIG. 3.** Plot of the complex viscosity \(\eta^* (\omega)\) as function of \(\omega\) 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 \(\eta'\) than for \(\eta''\) and becomes more prominent as \(p \to p_c\).

Finally, in Figure 4 we show the dimensionless self-diffusion constant \(\sqrt{m/\sigma^2 k_B T D}\) obtained from the velocity-velocity correlator [3] 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 \(D(L \to \infty, p \to p_c)\) 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
infinite cluster 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 $D$.

![Graph](image)

**FIG. 4.** The dimensionless diffusion constant $D(L,p)$ as function of $p$. The straight line corresponds to a power law $(p_c - p)^{0.7}$. 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. simulated a very different model, namely particles confined to the sites of a lattice and randomly crosslinked 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.

In conclusion, we have obtained the shear viscosity of a viscoelastic liquid below the gel point for a conceptually simple model that we have previously studied in the rigid phase. We have presented evidence that the shear viscosity diverges with an exponent $s \approx 0.7$ consistent with recent theoretical work [10] and some of the experimental data [3]. Future extensions of this work will include an investigation of viscoelasticity in two dimensions and a study of dynamics in the gel phase.

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