Anomalous stress relaxation in random macromolecular networks

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Abstract

Within the framework of a simple Rouse-type model we present exact analytical results for dynamical critical behaviour on the sol side of the gelation transition. The stress-relaxation function is shown to exhibit a stretched-exponential long-time decay. The divergence of the static shear viscosity is governed by the critical exponent $k = \phi - \beta$, where $\phi$ is the (first) crossover exponent of random resistor networks, and $\beta$ is the critical exponent for the gel fraction. We also derive new results on the behaviour of normal stress coefficients.

1 Introduction

The viscoelastic properties of incipient gels have received considerable interest, but are still controversial. Whereas the static critical behaviour as predicted by percolation theory has been confirmed in experiment as well as simulation [1], the dynamic critical behaviour, and in particular stress relaxation is much less understood. Conceptually, the experimental procedure is depicted in Figs. 1 and 2: a homogeneous, time-dependent shear flow is imposed, and the stress relaxation is measured. Throughout the sol phase, even far away from the critical point, one observes an anomalous time decay of the shear-stress relaxation function, which follows a stretched-exponential law $\exp\{-t/t^*\alpha\}$. However the exponent values [2–7] vary over a wide range, and in some experiments even non-universal exponents are reported, depending for example on molecular weight or concentration of crosslinks. Similarly, the divergence of the static shear viscosity is still a matter of debate. Experiments yield wide

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ranges of exponent values \([8,5,9]\) whose origin is not clear. Even the existence of a single dynamic universality class has been questioned \([8]\).

From a theoretical point of view, the issue is not clear either. Scaling arguments which are based on simple physical pictures or analogies to other random systems, are in conflict with each other. For example, it has been argued \([10]\) that the static shear viscosity \(\eta_n\) of a cluster of \(n\) polymers should be determined by the longest relaxation time \(t_n\) of the cluster. The latter has been identified with the time scale for diffusion of the cluster over a distance corresponding to its own size: \(t_n \propto R_n^2/D_n\). Here \(R_n\) denotes the radius of gyration that is assumed to scale with the mass of the cluster as \(R_n \propto n^{1/d_f}\) with \(d_f\) the Hausdorff-Besicovich dimension. In a simple Rouse model the diffusion constant behaves as \(D_n \propto 1/n\). The probability to find a cluster of size \(n\) is taken from percolation theory to yield \(\eta \propto \varepsilon^{-k}\) with \(k = 2\nu - \beta\). Here \(\varepsilon\) denotes the distance from the critical point and \(\nu\) and \(\beta\) are the exponents of percolation theory for the correlation length and the gel fraction, respectively.

In another line of approach one has tried to relate the viscosity to random resistor networks. For example, it was suggested \([11]\) that the conductivity of a random mixture of conductors and superconductors should show the same critical behaviour as the viscosity, \(s = k\).

In this Paper we discuss Rouse dynamics in an externally imposed shear flow, generalised to include the effects of random, permanent crosslinks. Within this model we have recently found \([12,13]\) the exact result \(k = \phi - \beta\) for the critical divergence of the static shear viscosity. Here \(\phi\) is the (first) crossover exponent for random resistor networks, which is discussed e.g. in \([14,15]\). This analytical result is in contradiction with all previous scaling arguments, but agrees with that of a molecular-dynamics simulations \([16]\). The afore-mentioned scaling arguments fail, because they ignore the multi-fractal structure of percolation clusters – as first noted by Cates \([17]\). To account for multi-fractality one needs to introduce another fractal dimension, the spectral dimension \(d_s\), which is independent of \(\beta\) and \(\nu\). The crossover exponent \(\phi\) is related to \(d_s\) according to \(\phi = \nu d_f[(2/d_s) - 1]\) so that our result \(k = \phi - \beta\) is incompatible with the proposal \(k = 2\nu - \beta\). It is also incompatible with the other suggestion \(s = k\), as can be seen most easily in \(d = 2\), where duality implies \(s = \phi\) \([18]\).

Whereas for Newtonian fluids the simple shear flow of Fig. 2 gives rise only to a shear stress \(\sigma_{xy}\), it is well known that in a non-Newtonian fluid all six components of the stress tensor are non-zero \([19]\). If the fluid is incompressible and isotropic, there are three independent, experimentally observable stress components: the shear stress \(\sigma_{xy}\), the first normal stress difference \(\sigma_{xx} - \sigma_{yy}\) and the second normal stress difference \(\sigma_{yy} - \sigma_{zz}\). We compute the normal stress coefficients \(\Psi_1\) and \(\Psi_2\) and find \(\Psi_2 = 0\), a characteristic result for Rouse-type models. The first normal stress coefficient \(\Psi_1\) is predicted to have a much stronger divergence than the shear viscosity as the gelation transition is ap-
proached. Even though one has performed many experiments [20] on both the shear-rate dependence of normal stresses in entangled or (temporarily) crosslinked polymeric liquids and on the time dependence of the normal-stress response to particular shapes of shear strain, we are not aware of any experiments measuring $\Psi_1$ as a function of the crosslink concentration. Previous theoretical work [21] relates the critical divergence of $\Psi_1$ at the gelation transition to scaling properties of the relaxation-time spectrum, see also [22] for a recent approach in a similar spirit.

Finally, we present a result on the long-time decay of the shear-stress relaxation function. We show that this decay is described by a stretched exponential, which is determined by the soft-mode excitations of the clusters, see [23] for details.

2 Model and Observables

We consider a fluid of $N$ identical molecular units each consisting of $L$ monomers. Examples are chains or rings of length $L$ or stars with $(L-1)$ branches. Within the Rouse-type model studied in this Paper it turns out that the critical behaviour as well as the anomalous long-time decay in the sol phase is independent of the internal structure of the molecular units. We therefore only discuss the simplest case in detail, namely molecular units which are just monomers, corresponding to $L = 1$. The reader who is interested in results for more complex molecular units is referred to [12,13].

The thermal degrees of freedom are the positions $\mathbf{R}_i(t), i = 1, \ldots, N$, of the monomers, which relax in the presence of $M$ quenched, random crosslinks, each connecting a pair $(i_e, i'_e), e = 1, \ldots, M$, of monomers. Crosslinks are modelled as harmonic springs

$$U := \frac{3}{2a^2} \sum_{e=1}^{M} \lambda_e (\mathbf{R}_{i_e} - \mathbf{R}_{i'_e})^2,$$

(1)
with random spring constants $\lambda_e$ and an overall coupling strength determined by the length $a > 0$. It is advantageous to express the potential energy in terms of the connectivity matrix $\Gamma$

$$\Gamma_{ii'} := \sum_{e=1}^{M} \lambda_e (\delta_{ii_e} - \delta_{ii'_e})(\delta_{ii'_i} - \delta_{ii'_i})$$

(2)

according to

$$U = \frac{3}{2a^2} \sum_{i,i'=1}^{N} \Gamma_{ii'} \mathbf{R}_i \cdot \mathbf{R}_{i'}.$$ 

(3)

A specific realisation of crosslinks is represented as a graph $\mathcal{G} = \{i_e, i'_e\}_{e=1}^{M}$ or, equivalently, by its connectivity matrix $\Gamma$. A simple example is shown in Fig. 3.

We consider Rouse dynamics generalised to include the effects of permanent random crosslinks [24–26] and an externally applied velocity field $\mathbf{v}_{\text{ext}}(\mathbf{r}, t)$

$$\zeta \left[ \partial_t R^\alpha_i(t) - v^\alpha_{\text{ext}}(\mathbf{R}_i(t), t) \right] = -\frac{\partial U}{\partial R^\alpha_i}(t) + \xi^\alpha_i(t).$$

(4)

Here, Greek indices label Cartesian coordinates $x, y$ or $z$. Inertial terms are neglected in (4), and friction with a friction constant $\zeta$ occurs when the velocity of a monomer deviates from the externally applied flow field. The crosslinks exert a force $-\partial U/\partial \mathbf{R}_i$ on the monomers, in addition to a random, fluctuating thermal-noise force with zero mean and covariance $\langle \xi^\alpha_i(t)\xi^\beta_{i'}(t') \rangle = 2\zeta \delta_{\alpha\beta}\delta_{ij}\delta(t-t')$. Note that we have chosen units in which the inverse temperature is equal to one.

In the sequel we will only be interested in a homogeneous linear shear flow

$$v^\alpha(\mathbf{r}, t) := \delta_{\alpha x} \kappa(t) y$$

(5)
with a time-dependent shear rate $\kappa(t)$, which is sketched in Fig. 2. Given this shear flow, the equation of motion (4) is linear and can be solved exactly for each realisation of the thermal noise [13].

In reaction to the externally applied shear flow, the crosslinked polymer system exhibits stress, whose tensor components are given in terms of a force-position correlation [24,25]

$$\sigma_{\alpha\beta}(t) = \lim_{t_0 \to -\infty} \frac{\rho_0}{V} \sum_{i=1}^{N} \left\langle \frac{\partial U}{\partial R_i^\alpha}(t) R_i^\beta(t) \right\rangle.$$  \hspace{1cm} (6)

Here, $\rho_0$ denotes the density of monomers, and the initial values are to be taken at more and more distant times $t_0$ in the past in order to ensure that after averaging over the thermal noise, the system has reached a steady state at time $t$. This yields for the stress tensor

$$\sigma(t) = \chi(0)1 + \int_{-\infty}^{t} dt' \chi(t - t') \kappa(t') \begin{pmatrix} 2 \int_{t'}^{t} ds \kappa(s) 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$  \hspace{1cm} (7)

confer [13], where the stress relaxation function is given by

$$\chi(t) = \frac{\rho_0}{N} \text{Tr} \left( [1 - E_0(G)] \exp \left\{ -\frac{6t}{\zeta a^2} \Gamma(G) \right\} \right),$$  \hspace{1cm} (8)

and the dependence of $\Gamma$ on the crosslink realisation $G$ has been emphasised in the notation. In (8), $E_0$ denotes the projector on the space of zero eigenvalues of $\Gamma$. These zero eigenvalues correspond to translations of whole clusters. The associated eigenvectors are constant within one cluster and zero outside. In the example of Fig. 3 the null space is spanned by the vectors $a_1 := 4^{-1/2}(1,1,1,1,0,0)$ and $a_2 := 2^{-1/2}(0,0,0,0,1,1)$, and one has $E_0 = a_1 a_1^\dagger + a_2 a_2^\dagger$. Within the simple Rouse model the zero eigenvalues do not contribute to the shear relaxation because there is no force acting between different clusters. The only contribution to stress relaxation is due to deformations of the clusters, as can be seen from (8). The long-time decay of $\chi$ will be dominated by the smallest eigenvalues of $\Gamma$, and we expect that anomalies in the long-time behaviour are due to a peculiar behaviour of the density of eigenvalues of $\Gamma$ for small eigenvalues.

To complete the definition of the dynamic model, we need to specify the distribution of random crosslinks. Two cases will be distinguished:
(i) Each pair of monomers is chosen with equal probability $c/N$, generating mean-field random graphs as discussed by Erdős and Rényi [27], see also [28]. As a function of crosslink concentration $c$, the system undergoes a percolation transition at a critical concentration $c_{\text{crit}} = \frac{1}{2}$. For $c < c_{\text{crit}}$ there is no macroscopic cluster, and almost all clusters are trees. The average number of tree clusters per particle is given in the macroscopic limit by

$$
\tau_n = \frac{n^{n-2}(2c e^{-2c})^n}{2cn!}.
$$

(9)

(ii) Crosslinks are distributed such that the cluster-size distribution follows a scaling law

$$
\tau_n = n^{-\tau}f((c_{\text{crit}} - c)n^\sigma)
$$

near criticality. This case includes both mean-field random graphs and random bond percolation.

For both cases (i) and (ii) we require the random spring constants $\lambda_e$ to be distributed independently from each other, as well as independently from the crosslink positions. Moreover, the probability for very soft spring constants to occur shall be sufficiently small in that sufficiently high inverse moments

$$
P_n := \int_0^\infty d\lambda \lambda^{-n}p(\lambda)
$$

(11)

of $\lambda_e$ are assumed to exist.

The combined average over crosslink configurations and random spring constants will be denoted by an overbar $\overline{\cdot}$. Using this notation, we implicitly assume that the macroscopic limit $N \to \infty$, $M \to \infty$, $M/N \to c$ is carried out, too.

3 Static shear viscosity

According to (7), a time-independent shear rate $\kappa(t) = \kappa$ induces a time-independent shear stress $\sigma_{xy} = \rho_0\eta\kappa$ which is determined by the static shear viscosity

$$
\eta := \int_0^\infty dt \chi(t) = \frac{\zeta a^2}{6N} \text{Tr} \left( \frac{1 - E_0}{\Gamma} \right).
$$

(12)
As mentioned before, the Rouse model does not include any interactions between different clusters so that the viscosity allows for a cluster decomposition. This is apparent in (12) from the block-diagonal structure of $\Gamma$. We decompose the graph $\mathcal{G}$ for a given crosslink realisation into $K$ connected clusters $\{\mathcal{N}_k\}_{k=1}^K$ with each cluster $\mathcal{N}_k$ containing $N_k$ monomers. The cluster decomposition of the viscosity then reads

$$\eta(\mathcal{G}) = \sum_{k=1}^K \frac{N_k}{N} \eta(\mathcal{N}_k).$$

(13)

In order to compute the viscosity of an arbitrary connected cluster $\mathcal{N}_k$, we exploit the analogy between a random network of harmonic springs with spring constants $\lambda_e$ and a random network of resistors of magnitude $1/\lambda_e$, see Fig. 4. Since both networks are governed by linear equations, it is plausible – and can be shown exactly [29] – that the resistance $\mathcal{R}(\mathcal{N}_k|i,j)$ between any two nodes $(i,j)$ in the cluster $\mathcal{N}_k$ can be expressed in terms of the pseudo-inverse of the connectivity matrix. This gives rise to the exact relation [13]

$$\eta(\mathcal{N}_k) = \frac{\zeta a^2}{12N_k^2} \sum_{i,j \in \mathcal{N}_k} \mathcal{R}(\mathcal{N}_k|i,j).$$

(14)

It remains to compute the average of the viscosity over all realisations of the crosslinks. For convenience, the average over different crosslink realisations is performed in two steps: We first average over all clusters of a given size $n$ and subsequently average over all cluster sizes with the appropriate cluster-size distribution $n\tau_n$,

$$\bar{\eta} = \sum_{n=2}^{\infty} n\tau_n \bar{\eta}_n.$$

(15)

Here, $\bar{\eta}_n$ is the average of the viscosity over all clusters of a given size $n$.

Fig. 4. Correspondence between a network of harmonic springs and of electrical resistors.
First, we consider the ensemble (i) of mean-field random graphs. For this case, all clusters are almost surely trees [27], and hence the resistance between any two nodes \((i, j)\) of a connected cluster is just their weighted chemical distance. For this reason, and due to the independence of the distribution of the \(\lambda_e\), \(\eta_n\) is known exactly [30]

\[
\eta_n = \frac{\zeta a^2}{12} P_1 (n - 1)! \sum_{\nu=2}^{n} \frac{n^{-\nu}(\nu - 1)}{(n-\nu)!} n^{-\nu}(n-\nu)! \]

(16)

with \(P_1\) being defined in (11). Together with the appropriate cluster-size distribution (9) we find [13]

\[
\bar{\eta} = \frac{\zeta a^2}{24c} P_1 \left[ \ln \left( \frac{1}{1-2c} \right) - 2c \right].
\]

(17)

Fig. 5 displays \(\eta\) in units of \(\zeta a^2/3\) as a function of \(c\) for the special case \(P_1 = 1\). The exact result (17) is valid for all \(0 < c < c_{\text{crit}} = \frac{1}{2}\) and exhibits a logarithmic divergence as the percolation transition is approached.

Second, we consider more general percolation ensembles which are only required to allow for a scaling description (10) close to criticality. Here we also assume that all spring constants are fixed, \(\lambda_e = 1\) for \(e = 1, \ldots, M\). The theory of random resistor networks [14,15] has established a scaling relation

\[
\left< \frac{1}{\mathcal{N}_k} \sum_{i,j \in \mathcal{N}_k} \mathcal{R}(\mathcal{N}_k | i, j) \right> \sim (c_{\text{crit}} - c)^{-(2-\eta)(\nu-\phi)}
\]

(18)
for the resistance which implies [13] via Eq. (14) an analogous scaling relation for the viscosity $\langle \eta \rangle_n \sim n^{\sigma \phi}$ with $\phi$ being the (first) crossover exponent. Together with the scaling form (10) of the cluster-size distribution, we find [13] for the critical exponent of the viscosity

$$k = \phi - \beta.$$  

(19)

For mean-field percolation one has $\phi = \beta = 1$, and thus $k = 0$, in accordance with (17). For 3-dimensional bond percolation high-precision simulations [31] for $\phi$ yield $k \approx 0.71$, in good agreement with recent simulations [16].

4 Normal stress coefficients

The isotropic part of the stress tensor is not significant for the simple shear flow (5). Thus, we concentrate on the first and second normal stress differences $\sigma_{xx} - \sigma_{yy}$ and $\sigma_{yy} - \sigma_{zz}$, respectively. For a time-independent shear rate $\kappa = \kappa(t)$ it is customary to define first and second normal stress coefficients by

$$\Psi_1 := \frac{\sigma_{xx} - \sigma_{yy}}{\rho_0 \kappa^2}, \quad \Psi_2 := \frac{\sigma_{yy} - \sigma_{zz}}{\rho_0 \kappa^2}.$$  

(20)

One deduces immediately from (7) that $\Psi_2 = 0$, a characteristic result for Rouse-type models. In contrast, the first normal stress coefficient $\Psi_1$ is non-zero

$$\Psi_1 = \frac{1}{2} \left( \frac{\zeta a^2}{3} \right)^2 \frac{1}{N} \text{Tr} \left( \frac{1 - E_0}{\Gamma^2} \right)$$  

(21)

and independent of the shear rate $\kappa$. Introducing the (averaged) density

$$D(\gamma) := \frac{1}{N} \text{Tr} \left\{ (1 - E_0)\delta(\gamma - \Gamma) \right\}$$  

(22)

of non-zero eigenvalues of $\Gamma$, one gets for the crosslink average of (21)

$$\overline{\Psi}_1 = \frac{1}{2} \left( \frac{\zeta a^2}{3} \right)^2 \int_0^\infty d\gamma \frac{D(\gamma)}{\gamma^2}.$$  

(23)

The inverse second moment of $D$ was calculated in Eq. (38) of [23] for mean-field random graphs with the help of a replica approach. Thus, we infer the exact result
\[ \Psi_1 = \frac{1}{2} \left( \frac{\zeta a^2}{3} \right)^2 c \left[ -\frac{8c^3 - 6c^2 - 5c + 1}{30c(1 - 2c)^3} P_1^2 - \frac{4c^2 - 3c - 1}{24c(1 - 2c)^2} P_2 \\
+ \frac{5P_2 - 4P_1^2}{240c^2} \ln(1 - 2c) \right] , \]  

which is valid for all \( 0 < c < c_{\text{crit}} = \frac{1}{2} \). The moments \( P_n \) were defined in (11). The result (24) implies the critical divergence

\[ \Psi_1 \sim \left( \frac{\zeta a^2}{3} \right)^2 \frac{P_1^2}{240} (c_{\text{crit}} - c)^{-3} \]  

at the gelation transition, whereas for \( c \to 0 \) one has

\[ \Psi_1 = \left( \frac{\zeta a^2}{3} \right)^2 \frac{P_2}{8} c + O(c^2) . \]

Fig. 6 displays \( \Psi_1 \) in units of \( (\zeta a^2/3)^2 \) as a function of \( c \) for the special case \( P_1 = P_2 = 1 \).

5 Relaxation at finite frequencies

According to (8) and (22) the averaged time-dependent shear relaxation function \( \chi(t) \) is related to the density of non-zero eigenvalues of the connectivity matrix \( \Gamma \) by a Laplace transformation

\[ \chi(t) = \rho_0 \int_0^\infty \mathrm{d}\gamma D(\gamma) \exp\left\{ -\gamma \frac{6t}{\zeta a^2} \right\} . \]  

The eigenvalue density \( D(\gamma) \) has been discussed in detail in [23]: analytically for mean-field random graphs and numerically for finite-dimensional percolation. Here we just recall its most prominent feature for mean-field random graphs: \( D(\gamma) \) shows a Lifshits tail for small eigenvalues, as first suggested by Bray and Rodgers [32]

\[ D(\gamma) \sim \exp \left\{ -\left( \frac{\gamma_0 (1 - 2c)^3}{\gamma} \right)^{1/2} \right\} , \quad \gamma \downarrow 0, \quad c < \frac{1}{2} , \]  

provided the probability density \( p(\lambda) \) of the random spring constants \( \lambda_0 \) contains no Dirac delta functions and vanishes sufficiently fast at the origin (see [23] for details). In the context of gelation, the small-\( \gamma \)-behaviour (28) of \( D \)
gives rise to a stretched-exponential decay of the stress relaxation function 
\[ \chi(t) \sim \exp\{- (t/t^*)^{1/3}\} \] for long times. In other words, it is the soft-mode 
excitations of the clusters which determine the stress relaxation at low fre-
quencies.

6 Outlook

The understanding of dynamical critical behaviour at the gelation transition is 
currently far from being satisfactory. On the one hand, the experimental data 
– if existent – scatter widely and therefore do not allow for a serious check 
of theoretical predictions. On the other hand, theoretical results, as presented 
in this Paper within the framework of a simple Rouse-type model, are likely 
to be affected by shortcomings due to the neglect of certain interactions by 
the model itself. We only mention the excluded-volume interaction and the 
hydrodynamic interaction, both of which are believed to be of importance 
for stress relaxation. It is therefore one goal to incorporate effects of these 
interactions in future activities.

Second, it is desirable to extend the semi-microscopic approach advocated here 
to the dynamics of the gel phase. This will provide information about stress 
relaxation in the gel, in particular, the critical vanishing of the static shear modulus at the transition. Moreover, being a cluster of macroscopic size, the gel admits to ask new types of questions. For instance, as initiated in [33], one 
may examine the spatial extent of phonon-type excitations in this random 
network as a function of the excitation energy. This may reveal a localization-
delocalization transition, a well-known phenomenon from disordered systems 
of very different kinds.

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