

## Normal stresses at the gelation transition

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A simple Rouse-type model, generalized to incorporate the effects of chemical cross-links, is used to obtain a theoretical prediction for the critical behavior of the normal-stress coefficients  $\Psi_1$  and  $\Psi_2$  in polymeric liquids when approaching the gelation transition from the sol side. While the exact calculation shows  $\Psi_2 \equiv 0$ , a typical result for these types of models, an additional scaling ansatz is used to demonstrate that  $\Psi_1$  diverges with a critical exponent  $\ell = k + z$ . Here,  $k$  denotes the critical exponent of the shear viscosity and  $z$  the exponent governing the divergence of the time scale in the Kohlrausch decay of the shear-stress relaxation function. For cross-links distributed according to mean-field percolation, this scaling relation yields  $\ell = 3$ , in accordance with an exact expression for the first normal-stress coefficient based on a replica calculation. Alternatively, using three-dimensional percolation for the cross-link ensemble we find the value  $\ell \approx 4.9$ . Results on time-dependent normal-stress response are also presented.

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### I. INTRODUCTION

Chemical gelation is the process of randomly introducing cross-links between the constituents of a (macro) molecular fluid. One way to investigate the effects of the cross-links on the fluid dynamics consists in measuring the stresses that the cross-linked fluid builds up when subjected to a simple shear flow. For an incompressible, isotropic fluid one can experimentally access [1] three independent components of the stress tensor  $\boldsymbol{\sigma}$ : the shear stress  $\sigma_{xy}$  and the first and second normal-stress differences  $\sigma_{xx} - \sigma_{yy}$  and  $\sigma_{yy} - \sigma_{zz}$ . For static shear flows these give rise to three independent material functions: the shear viscosity  $\eta$  and the first and second normal-stress coefficients  $\Psi_1$  and  $\Psi_2$ . Generally speaking, both Newtonian and non-Newtonian fluids possess a nonvanishing shear viscosity. But, whereas for a Newtonian fluid both  $\Psi_1$  and  $\Psi_2$  are always zero, it is precisely the nonvanishing of  $\Psi_1$  that explains a number of characteristic effects known for example polymeric liquids [2], see also Sec. 2.3 in Ref. [1]. On the other hand, even for non-Newtonian fluids  $\Psi_2$  is typically found to be very small as compared to  $\Psi_1$ , and the “Weissenberg hypothesis,”  $\Psi_2 = 0$ , is a good approximation in these cases [2]. It also seems that  $\Psi_2$  is not as well-investigated experimentally as  $\Psi_1$ .

In the context of gelation one is particularly interested in the dependence of these stresses on the cross-link concentration  $c$ . Universal critical behavior is expected to occur at the gelation transition, that is, at the critical concentration  $c_{\text{crit}}$ , where the fluid (sol) undergoes a phase change into an amorphous solid state (gel). As far as shear stress is concerned, there exist numerous experimental investigations on the static shear viscosity and on the time-dependent shear-stress-relaxation function. The experimentally measured values for the critical exponent  $k$ , which governs the algebraic divergence of the shear viscosity when approaching  $c_{\text{crit}}$  from the

sol side, scatter considerably and are found in the range  $k \approx 0.6$ – $1.7$ , see e.g. Refs. [3–8]. The origin of this wide spread is controversially discussed and not yet understood. From a theoretical point of view there exists a bunch of competing and partially contradicting scaling relations that express  $k$  in terms of percolation exponents. Each of them relies on heuristic arguments whose validity is mostly unclear. We refer the reader to [9,10] for a summary and references. Here we only mention the scaling relation  $k = 2\nu - \beta$  that was first proposed by de Gennes [11] and rederived by many others. Erroneously, it is generally referred to as the “Rouse expression” for the viscosity exponent. Here,  $\nu$  is the exponent governing the divergence of the correlation length and  $\beta$  is associated with the gel fraction. For three-dimensional bond percolation one would get the value  $(2\nu - \beta)|_{d=3} \approx 1.35$ . Recently, the viscosity was *exactly* determined within the Rouse model for gelation in Refs. [9,10]. The analysis disproves the above result and shows that

$$k = \phi - \beta \quad (1)$$

is the true scaling relation valid for Rouse dynamics. Here,  $\phi$  denotes the first crossover exponent of a corresponding random resistor network [12,13]. When inserting high-precision data [14,15] for  $\phi$  and  $\beta$  obtained from three-dimensional bond percolation, the true Rouse value of the viscosity exponent turns out to be  $(\phi - \beta)|_{d=3} \approx 0.71$  and agrees with simulations [16] on a similar model. The discrepancy to de Gennes’ result above can be attributed to the neglect of the *multifractal* nature of percolation clusters in Ref. [11]. Amazingly, the true Rouse value  $k|_{d=3} \approx 0.71$  differs only little from that of another proposal,  $k = s$ , by de Gennes [17], where he alluded to an analogy to the conductivity exponent  $s|_{d=3} \approx 0.73$  of an electrical network consisting of a random mixture of superconductors and normal conductors. This close agreement, however, is coincidental, as can be seen from corresponding results in two dimensions.

In contrast, we are not aware of any experimental or theoretical studies concerning the dependence on the cross-link concentration  $c$  of normal stresses near the gelation transi-

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tion. This seems all the more surprising since there exist many experiments [18–21] on both the shear-rate dependence of normal stresses in entangled or (temporarily) cross-linked polymeric liquids in order to explain shear-thinning or shear-thickening phenomena and on the time dependence of the normal-stress response to particular shapes of shear strain. Theoretical explanations of these experimental findings mainly rely on the analysis of transient network models, see e.g. Refs. [22–25].

Even though Rouse-type models incorporate no other physical interactions between monomers apart from connectivity, they serve as a standard theoretical reference in terms of which experimental data are frequently interpreted. Therefore, it is important to test their predictions as accurately as possible. In this paper, we use the same generalized Rouse-type model as in Refs. [9,10,26] to predict the critical behavior of the normal-stress coefficients  $\Psi_1$  and  $\Psi_2$  when approaching the gelation transition from the sol side. Within this model it will turn out that  $\Psi_2$  vanishes for all  $c$  and that  $\Psi_1$  diverges with a critical exponent

$$\ell = k + z \quad (2)$$

when approaching  $c_{\text{crit}}$  from the sol side. Here,  $z$  denotes the exponent governing the divergence of the time scale in the Kohlrausch decay of the shear-stress relaxation function. For cross-links distributed according to mean-field percolation (also called “classical theory”), this scaling relation yields  $\ell = 3$ , in accordance with an exact expression for  $\Psi_1$  based on a replica calculation. Alternatively (and more realistically), using three-dimensional percolation for the cross-link ensemble we find the value  $\ell \approx 4.9$ . Thus, the model predicts a much more pronounced divergence of  $\Psi_1$  as compared to  $\eta$  so that  $\Psi_1$  may serve as a sensitive indicator for the gelation transition. We also derive results on the time-dependent normal-stress response. In particular, the Lodge-Meissner rule, see, e.g., Sec. 3.4.e in Ref. [1], is shown to hold for normal-stress relaxation after a sudden shearing displacement.

We hope that these theoretical investigations motivate corresponding experimental work in order to develop more insight on normal stresses in gelling polymeric liquids.

## II. MODEL

We follow a semimicroscopic approach to gelation based on a Rouse-type model for  $N$  monomers. The monomers are treated as point particles with positions  $\mathbf{R}_i(t)$ ,  $i = 1, \dots, N$ , in three-dimensional space. The motion of the monomers is constrained by  $M$  randomly chosen, harmonic cross-links that connect the pairs  $(i_e, i'_e)$ ,  $e = 1, \dots, M$ , of monomers and give rise to the potential energy

$$U := \frac{3}{2a^2} \sum_{e=1}^M \lambda_e (\mathbf{R}_{i_e} - \mathbf{R}_{i'_e})^2 =: \frac{3}{2a^2} \sum_{i,j} \Gamma_{ij} \mathbf{R}_i \cdot \mathbf{R}_j. \quad (3)$$

Here, the fixed length  $a > 0$  models the overall inverse coupling strength, whereas the individual coupling constants  $\lambda_e$  are chosen at random. Quite often, only the special case  $\lambda_e$

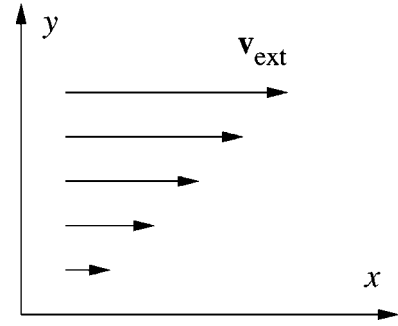


FIG. 1. Homogeneous linear shear flow (5).

$= 1$  has been considered previously. The second equality in Eq. (3) introduces the random  $N \times N$  connectivity matrix, which encodes all properties of a given cross-link realization.

Following Refs. [27–29] we employ a simple relaxational dynamics

$$\zeta [\partial_t \mathbf{R}_i^\alpha(t) - v_{\text{ext}}^\alpha(\mathbf{R}_i(t), t)] = -\frac{\partial U}{\partial \mathbf{R}_i^\alpha}(t) + \xi_i^\alpha(t) \quad (4)$$

without inertial term to describe the motion of the monomers in the externally applied velocity field

$$v_{\text{ext}}^\alpha(\mathbf{r}, t) := \delta_{\alpha x} \kappa(t) y \quad (5)$$

with a time-dependent shear rate  $\kappa(t)$ , see also Fig. 1. Here, Greek indices label Cartesian coordinates  $x$ ,  $y$ , or  $z$ . A friction force with friction constant  $\zeta$  applies if the velocity of a monomer deviates from the externally applied flow field. The cross-links exert a force  $-\partial U / \partial \mathbf{R}_i$  on the monomers, in addition to a random, fluctuating thermal-noise force obeying Gaussian statistics with zero mean and covariance  $\langle \xi_i^\alpha(t) \xi_j^\beta(t') \rangle = 2\zeta \delta_{\alpha\beta} \delta_{ij} \delta(t-t')$ . Note that we have chosen units in which the inverse temperature is equal to one. Given the shear flow (5), the equation of motion (4) is linear and can be solved exactly for each realization of the thermal noise [10].

To complete the description of the dynamic model, we have to specify the statistical ensemble that determines the realizations of the cross-links. We will distinguish two cases:

(i) Mean-field percolation (also called “classical theory”): each pair of monomers is chosen independently with equal probability  $M/N^2$ , irrespectively of the monomer positions in space. As a function of the cross-link concentration  $c := M/N$ , 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 [30,31].

(ii) Three-dimensional bond percolation [15,32].

For either case we assume the random coupling constants  $\lambda_e$  to be distributed independently of the cross-link configuration, as well as independently of each other with the same (smooth) probability distribution  $p(\lambda)$ . Moreover, sufficiently high inverse moments

$$P_n := \int_0^\infty d\lambda \lambda^{-n} p(\lambda) \quad (6)$$

of  $\lambda_e$  shall exist.

The combined average over cross-link configurations and random coupling constants will be denoted by an overbar. Using this notation, we implicitly assume that the macroscopic limit  $N \rightarrow \infty$ ,  $M \rightarrow \infty$ ,  $M/N \rightarrow c$  is carried out, too.

Before turning to the analysis of the model, we would like to comment on the fact that it describes the random cross-linking of single monomers rather than of preformed polymers. However, this does not mean that the applicability of the model is limited to the description of random network built up by polycondensation from small structural units. Indeed, we expect from universality that details at small length scales are irrelevant for the true critical behavior at the gelation transition so that these results will also hold for random network built from arbitrary macromolecules, as is the case in vulcanization, for example. This general universality argument was confirmed [10] by explicit computations of the critical behavior of the shear viscosity with the mean-field distribution of cross-links.

### III. STRESS TENSOR AND NORMAL-STRESS COEFFICIENTS

Due to the externally applied shear flow the cross-links exert shear stress on the polymer system, whose tensor components are given in terms of a force-position correlation [27,28],

$$\sigma_{\alpha\beta}(t) = \lim_{t_0 \rightarrow -\infty} \frac{\rho_0}{N} \sum_{i=1}^N \left\langle \frac{\partial U}{\partial R_i^\alpha}(t) R_i^\beta(t) \right\rangle. \quad (7)$$

Here,  $\rho_0$  denotes the density of monomers. In Eq. (7) one has to insert the explicitly known [10] solutions  $\mathbf{R}_i(t)$  of the Rouse equation (4) at time  $t$  with initial data  $\mathbf{R}_i(t_0)$  at time  $t_0$ . In order to ensure that the thermal-noise average allows for the description of a possible stationary state of the system at finite times  $t$ , the time evolution is chosen to start in the infinite past,  $t_0 \rightarrow -\infty$ , thereby losing all transient effects that stem from the initial data. This yields [10] for the stress tensor

$$\boldsymbol{\sigma}(t) = \chi(0) \mathbf{1} + \int_{-\infty}^t dt' \chi(t-t') \boldsymbol{\kappa}(t') \times \begin{pmatrix} 2 \int_{t'}^t ds \kappa(s) & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (8)$$

where  $\mathbf{1}$  denotes the  $3 \times 3$  unit matrix and the stress-relaxation function is given by

$$\chi(t) := \frac{\rho_0}{N} \text{Tr} \left[ (1 - E_0) \exp \left( - \frac{6t}{\zeta a^2} \Gamma \right) \right]. \quad (9)$$

The symbol Tr in Eq. (9) stands for the trace over  $N \times N$  matrices, and  $E_0$  denotes the projector on the space of zero eigenvalues of  $\Gamma$ , which correspond to translations of whole

clusters. The associated eigenvectors are constant within each cluster and zero outside [10,33]. Within the simple Rouse model the zero eigenvalues do not contribute to shear relaxation because there is no force acting between different clusters. The only contribution to stress relaxation is due to deformations of the clusters.

For a time-independent shear rate  $\kappa(t) \equiv \kappa$  it is customary to define a first and second normal-stress coefficient by

$$\Psi_1 := \frac{\sigma_{xx} - \sigma_{yy}}{\rho_0 \kappa^2}, \quad \Psi_2 := \frac{\sigma_{yy} - \sigma_{zz}}{\rho_0 \kappa^2}. \quad (10)$$

One deduces immediately from Eq. (8) that

$$\Psi_2 = 0, \quad (11)$$

a characteristic result for Rouse-type models. In contrast, the first normal-stress coefficient  $\Psi_1$  is nonzero

$$\Psi_1 = \frac{1}{2} \left( \frac{\zeta a^2}{3} \right)^2 \frac{1}{N} \text{Tr} \left( \frac{1 - E_0}{\Gamma^2} \right) \quad (12)$$

and independent of the shear rate  $\kappa$ .

For a macroscopic system  $\Psi_1$  is expected to be a self-averaging quantity. Therefore, we will calculate the disorder average of Eq. (12) over all cross-link realizations and all cross-link strengths. To do so it is convenient to introduce the averaged density

$$D(\gamma) := \frac{1}{N} \text{Tr} [(1 - E_0) \delta(\gamma - \Gamma)] \quad (13)$$

of nonzero eigenvalues of  $\Gamma$ . Physically,  $D$  describes the distribution of relaxation rates in the network in units of  $6/(\zeta a^2)$ , as is evident from the representation

$$\bar{\chi}(t) = \rho_0 \int_0^\infty d\gamma \exp \left\{ - \frac{6t\gamma}{\zeta a^2} \right\} D(\gamma) \quad (14)$$

of the disorder average of the stress-relaxation function (9). Various properties of the eigenvalue density  $D$  are discussed in detail in Ref. [26]. The average  $\bar{\Psi}_1$  now appears as the second inverse moment of  $D$ ,

$$\bar{\Psi}_1 = \frac{1}{2} \left( \frac{\zeta a^2}{3} \right)^2 \int_0^\infty d\gamma \frac{D(\gamma)}{\gamma^2}, \quad (15)$$

while the disorder-averaged static shear viscosity  $\bar{\eta} := \bar{\sigma}_{xy}/(\rho_0 \kappa)$  is determined [9,10] by the first inverse moment

$$\bar{\eta} = \frac{1}{\rho_0} \int_0^\infty dt \bar{\chi}(t) = \frac{\zeta a^2}{6} \int_0^\infty d\gamma \frac{D(\gamma)}{\gamma}. \quad (16)$$

At this point one can already see that  $\bar{\Psi}_1$  serves as a sensitive indicator for the gelation transition. Indeed, the Jensen inequality [34] implies

$$\bar{\Psi}_1 \geq \frac{2(\bar{\eta})^2}{\int_0^\infty d\gamma D(\gamma)} \geq 2(\bar{\eta})^2, \quad (17)$$

and hence

$$\ell \geq 2k \quad (18)$$

with  $\ell$  denoting the critical exponent of  $\bar{\Psi}_1 \sim (c_{\text{crit}} - c)^{-\ell}$  and  $k$  denoting that of  $\bar{\eta} \sim (c_{\text{crit}} - c)^{-k}$ .

In the two following sections we will determine the precise Rouse value of  $\ell$  for the two different types of cross-link ensembles described above.

#### IV. MEAN-FIELD PERCOLATION

For mean-field random graphs (i) the second inverse moment of the eigenvalue density  $D$  was calculated in Eq. (38) of Ref. [26] with the help of a replica approach. This gives rise to the exact result

$$\bar{\Psi}_1 = \frac{1}{2} \left( \frac{\zeta a^2}{3} \right)^2 c \left[ -\frac{8c^3 - 6c^2 - 5c + 1}{30c(1-2c)^3} P_1^2 - \frac{4c^2 - 3c - 1}{24c(1-2c)^2} P_2 + \frac{5P_2 - 4P_1^2}{240c^2} \ln(1-2c) \right], \quad (19)$$

which is valid for all  $0 < c < c_{\text{crit}} = \frac{1}{2}$ . The inverse moments  $P_n$  were defined in Eq. (6). From Eq. (19) we read off the critical divergence

$$\bar{\Psi}_1 \sim \left( \frac{\zeta a^2}{3} \right)^2 \frac{P_1^2}{240} \varepsilon^{-3}, \quad \varepsilon := c_{\text{crit}} - c \downarrow 0 \quad (20)$$

at the gelation transition, and hence the critical exponent

$$\ell = 3. \quad (21)$$

For  $c \rightarrow 0$  one expands

$$\bar{\Psi}_1 = \left( \frac{\zeta a^2}{3} \right)^2 \frac{P_2}{8} c + \mathcal{O}(c^2). \quad (22)$$

Figure 2 displays  $\bar{\Psi}_1$  in units of  $(\zeta a^2/3)^2$  as a function of  $c$  for the special case  $P_1 = P_2 = 1$ .

It is the merit of the mean-field percolation ensemble that it allows for a variety of exact analytical calculations. However, since the probability for a cross-link to occur does not depend on the monomers' positions in space, this ensemble is believed to provide a fairly unrealistic description for three-dimensional gels. For this reason we consider an alternative cross-link ensemble in the following section, which has been successfully used [35] to explain static properties of polymer systems.

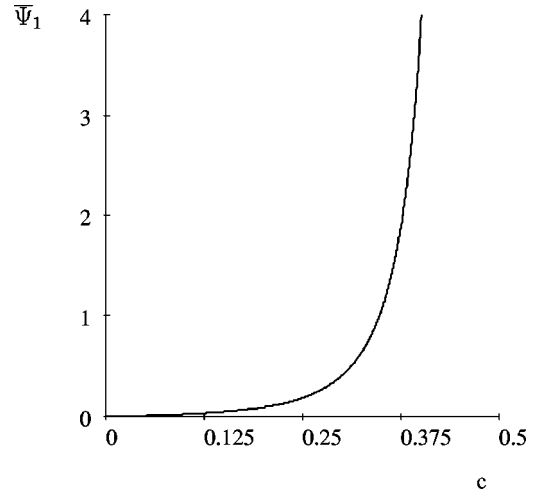


FIG. 2. First normal-stress coefficient (19) in units of  $(\zeta a^2/3)^2$  as a function of  $c$  for  $P_1 = P_2 = 1$ .

#### V. THREE-DIMENSIONAL BOND PERCOLATION

For this ensemble of cross-links the second inverse moment (15) of the eigenvalue density  $D_\varepsilon$ —note that in this section we emphasize the dependence on  $\varepsilon := c_{\text{crit}} - c$  in the notation of various quantities—is not known analytically. In order to proceed we assume that  $D_\varepsilon$  follows a scaling law

$$D_\varepsilon(\gamma) \sim \gamma^{\Delta-1} f[\gamma^*(\varepsilon)/\gamma] \quad (23)$$

close to the critical point and for small enough  $\gamma$ . It is determined by a typical relaxation rate  $\gamma^*(\varepsilon) \sim \varepsilon^z$ , which vanishes when approaching the critical point, and a scaling function  $f(x)$  that tends to a nonzero constant for  $x \rightarrow 0$  and decays faster than any inverse polynomial for  $x \rightarrow \infty$ . In particular, this gives the power-law behavior  $D_{\varepsilon=0}(\gamma) \sim \gamma^{\Delta-1}$  asymptotically for  $\gamma \rightarrow 0$  at criticality, in agreement with experiments [36,37]. The measured exponent values, however, scatter considerably,  $\Delta \approx 0.4-0.8$ , and seem to depend on the mass of the cross-linked molecules [38]. Note that on general grounds the exponent  $\Delta$  has to be positive, because otherwise  $D_{\varepsilon=0}(\gamma)$  would not be integrable at  $\gamma=0$ , in contradiction to the definition (13). The scaling law (23) yields, via the Laplace transform (14), the scaling law

$$\bar{\chi}_\varepsilon(t) \sim \varepsilon^{z\Delta} g[t/\tau^*(\varepsilon)] \quad (24)$$

for the long-time behavior of the stress-relaxation function. Here, the scaling function obeys  $g(x) \sim x^{-\Delta}$  for  $x \rightarrow 0$  and the typical relaxation time  $\tau^*(\varepsilon) := \zeta a^2 / [6\gamma^*(\varepsilon)] \sim \varepsilon^{-z}$  diverges when approaching the critical point. Precisely at the critical point one finds an algebraic long-time decay  $\bar{\chi}_{\varepsilon=0}(t) \sim t^{-\Delta}$ . Dynamical scaling relates  $\Delta$  to  $z$  and to the exponent  $k$  of the shear viscosity

$$\Delta = (z - k)/z, \quad (25)$$

see e.g. Refs. [26,38]. For  $x \rightarrow \infty$  the scaling function  $g(x)$  has to decay like a stretched exponential in order to accommodate the experimentally found [39] Kohlrausch decay



$$\bar{\chi}_{\varepsilon>0}(t) \sim \exp\{-[t/\tau^*(\varepsilon)]^\alpha\} \quad (26)$$

of the stress-relaxation function in the sol phase away from criticality, where  $\alpha$  is a noncritical and possibly nonuniversal exponent. We will return to Eq. (26) in the following section.

From Eqs. (15), (23), and (25) we deduce  $\bar{\Psi}_1 \sim \varepsilon^{-\ell}$  for  $\varepsilon \downarrow 0$  with an exponent given by the scaling relation

$$\ell = k + z = k \frac{2 - \Delta}{1 - \Delta}. \quad (27)$$

Since  $\Delta > 0$ , we have  $z > k$  and the scaling relation (27) is compatible with the inequality (18). Equation (27) was obtained previously in Ref. [40] from a model density of relaxation times with a sharp upper cutoff.

According to Eq. (1) the viscosity exponent  $k$  for the Rouse-type model under consideration is given by  $\phi - \beta$  and takes the value  $k \approx 0.71$ , when using three-dimensional bond percolation to generate the cross-link ensemble. Concerning  $\Delta$ , we are only aware of Ref. [26], where this exponent is determined for the Rouse model at hand without any further assumptions. It was done by numerical computations of the eigenvalue density (13) and yields  $\Delta \approx 0.83$ . But, as compared to the values for  $\phi$  and  $\beta$ , we suspect the numerical accuracy of the result for  $\Delta$  to be rather poor due to finite-size effects. Yet, using this value, Eq. (27) predicts

$$\ell \approx 4.9 \quad (28)$$

for the exponent of the first normal-stress coefficient  $\bar{\Psi}_1$ . If, instead, one ignored the *multifractal* structure of percolation clusters in employing the wrong scaling relations  $k = 2\nu - \beta$  and  $t = d\nu$ , where  $t$  is the critical exponent of the elastic modulus in the gel phase, one would arrive [41] at the value  $\Delta \approx 0.66$ . This would yield the considerably lower result  $\ell \approx 2.8$ . Thus, it is of importance to improve the accuracy of the exact numerical computation of  $\Delta$  within the Rouse model.

Finally, we would like to point out that for mean-field percolation the scaling relation (27) is consistent with the exact result presented in the preceding section. For, in this case the model yields  $k = 0$  [9,10],  $z = 3$ , and  $\Delta = 1$  [26], and thus (27) gives  $\ell = 3$  in accordance with Eq. (21).

## VI. TIME-DEPENDENT NORMAL-STRESS RESPONSE

First, let us focus on the normal-stress response to the inception of a steady shear flow  $\kappa(t) = \kappa_0 \Theta(t)$ . Here  $\Theta$  de-

notes the Heaviside unit step function. For each realization of the cross-links Eq. (8) leads to

$$N_1(t) := \sigma_{xx}(t) - \sigma_{yy}(t) = 2\kappa_0^2 \int_0^t dt' t' \chi(t') \quad (29)$$

in accordance with the principle of frame invariance [42]. Equations (9) and (12) then imply that for all cross-link concentrations below  $c_{\text{crit}}$  the first normal-stress difference increases towards its steady-state value like a stretched exponential

$$\bar{N}_1(t) = \rho_0 \kappa_0^2 \bar{\Psi}_1 - 2\kappa_0^2 \int_t^\infty dt' t' \bar{\chi}(t') \quad (30)$$

with the same exponent  $\alpha$  as the shear-relaxation function (26). In contrast, for  $c = c_{\text{crit}}$  we deduce from Eq. (29) the algebraic growth  $\bar{N}_1(t) \sim t^{2-\Delta}$  for long times, a result already known on a more phenomenological basis [38].

Second, we consider a sudden shearing displacement  $\kappa(t) = E \delta(t)$ , where  $\delta$  denotes the Dirac-delta function. From Eq. (8) we infer

$$N_1(t) = \int_0^\infty dt' \chi(t') \frac{d}{dt'} \left[ \int_{t-t'}^t ds \kappa(s) \right]^2 = E^2 \chi(t), \quad (31)$$

which, after averaging over disorder, amounts to the Kohlrausch decay (26) in the long-time limit for systems below the critical point, respectively, to the algebraic decay  $t^{-\Delta}$  for  $c = c_{\text{crit}}$ . Upon comparing (31) to the corresponding result  $\sigma_{xy}(t) = E \chi(t)$  for shear stress, the Lodge-Meissner rule  $N_1(t)/\sigma_{xy}(t) = E$ , see e.g., Sec. 3.4.e in Ref. [1], holds for each cross-link realization in this Rouse-type model.

Third, we consider the double-step strain flow  $\kappa(t) = E \delta(t) - E \delta(t - t_1)$  with  $t > t_1 > 0$ . In this case one can verify in an analogous manner the corresponding relation  $N_1(t)/\sigma_{xy}(t) = -E$ , which is known [21] to be valid for class I simple fluids.

## VII. OUTLOOK

We hope to stimulate detailed experimental investigations on the cross-link dependence of normal stresses in polymeric liquids close to the gelation transition. If such experimental results were at hand, one could judge the effects of the simplifications that underlie the above Rouse-type model, such as the neglect of the excluded-volume interaction and of the hydrodynamic interaction.

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