Normal stresses at the gelation transition

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A simple Rouse-type model, generalised to incorporate the effects of chemical crosslinks, is used to obtain a theoretical prediction for the critical behaviour of the normal-stress coefficients \( \Psi_1 \) and \( \Psi_2 \) at the gelation transition. 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 crosslinks 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 crosslink 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 crosslinks between the constituents of a (macro-) molecular fluid. One way to investigate the effects of the crosslinks on the fluid dynamics consists in measuring the stresses the crosslinked fluid builds up when subjected to a simple shear flow. For an incompressible, isotropic fluid one can experimentally access three independent components of the stress tensor \( \sigma \): 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 non-vanishing shear viscosity. But, whereas for a Newtonian fluid both \( \Psi_1 \) and \( \Psi_2 \) are always zero, it is precisely the non-vanishing of \( \Psi_1 \) that explains a number of characteristic effects known for e.g. polymeric liquids [1], see also §2.3 in [2]. 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 crosslink concentration \( c \). Universal critical behaviour is expected to occur at the gelation transition, that is, at the critical concentration \( c_{\text{crit}} \), where the fluid (sol) undergoes a sudden 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. [3, 4, 5, 6, 7, 8]. The origin of this wide spreading is controversially discussed and eventually unclear. From a theoretical point of view there exists a bunch of competing and partially contradicting scaling relations which express \( k \) in terms of percolation exponents. Each of them relies on heuristic arguments whose validity is mostly unclear. We refer the reader to [3, 9] for a summary and references. Here we only mention the scaling relation \( k = 2\nu - \beta \) which was first proposed by de Gennes [10] 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 to 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 [11, 12]. The analysis disproves the above result and shows that

\[
k = \phi - \beta
\]

is the true scaling relation valid for Rouse dynamics. Here, \( \phi \) denotes the first crossover exponent of a corresponding random resistor network [13, 14]. When inserting [13, 14] high-precision data 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 [14] 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 [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 [13], 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, seems to be coincidental.

In contrast, the authors are not aware of any experimental or theoretical studies concerning the dependence
on the crosslink concentration $c$ of normal stresses near the gelation transition. This seems all the more surprising since there exist many experiments \cite{13, 14, 24} on both the shear-rate dependence of normal stresses in entangled or (temporarily) crosslinked 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. \cite{20, 21, 22, 23}.

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 in terms of which experimental data are frequently interpreted since there exist many experiments \cite{16, 17, 18, 19} on the gelation transition. This seems all the more surprising.

\begin{equation}
\ell = k + z \tag{2}
\end{equation}

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 crosslinks 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 crosslink 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. \S3.4.e in \cite{3}, 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 (near) critical gels.

\section{II. Model}

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

\begin{equation}
U := \frac{3}{2a^2} \sum_{e=1}^{M} \lambda_e (\mathbf{R}_{ie} - \mathbf{R}_{ie'})^2 = \frac{3}{2a^2} \sum_{i,j}^{N} \Gamma_{ij} \mathbf{R}_i \cdot \mathbf{R}_j. \tag{3}
\end{equation}

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

Following \cite{25, 26, 27} we employ a simple relaxational dynamics

\begin{equation}
\zeta \left[ \partial_t R_i^\alpha(t) - v_{\text{ext}}^\alpha(t, \mathbf{R}_i(t), t) \right] = -\frac{\partial U}{\partial R_i^\alpha(t)} + \xi_i^\alpha(t) \tag{4}
\end{equation}

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

\begin{equation}
v_{\text{ext}}^\alpha(r, t) := \delta_{\alpha x} \kappa(t) y \tag{5}
\end{equation}

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 crosslinks 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 $\langle \xi_i^\alpha(t) \xi_j^{\alpha'}(t') \rangle = 2\zeta \delta_{\alpha \beta} \delta_{ij} \delta(t - t')$. Note that we have chosen units in which the inverse temperature is equal to one. Given the shear flow (3), the equation of motion (4) is linear and can be solved exactly for each realisation of the thermal noise (10).

To complete the description of the dynamic model, we have to specify the statistical ensemble which determines the realisations of the crosslinks. 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 crosslink concentration $c := M/N$, the system undergoes a percolation transition at a critical concentration $c_{\text{crit}} = 1/2$. For $c < c_{\text{crit}}$ there is
no macroscopic cluster, and almost all clusters are trees \(^{28, 29}\).

(ii) Three-dimensional bond percolation \(^{30, 31}\).

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

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

of \(\lambda_c\) shall exist.

The combined average over crosslink configurations and random coupling 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.

Before turning to the analysis of the model we would like to comment on the fact that it describes the random crosslinking 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 networks 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 behaviour at the gelation transition so that these results will also hold for random networks 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 behaviour of the shear viscosity with the mean-field distribution of crosslinks.

III. STRESS TENSOR AND NORMAL-STRESS COEFFICIENTS

Due to the externally applied shear flow the crosslinks exert shear stress on the polymer system, whose tensor components are given in terms of a force-position correlation \(^{25, 26}\)

\[
s_{\alpha\beta}(t) = \lim_{t_0 \to -\infty} \frac{\rho_0}{N} \sum_{i=1}^N \left\langle \frac{\partial U}{\partial R_i^\alpha} \left( \frac{\partial U}{\partial R_i^\beta} \right) \right\rangle.
\]

Here, \(\rho_0\) denotes the density of monomers. In \(^{10}\) one has to insert the explicitly known \(^{10}\) solutions \(R_i(t)\) of the Rouse equation \(^{8}\) at time \(t\) with initial data \(R_i(t_0)\) 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, \(t_0 \to -\infty\), thereby losing all transient effects which stem from the initial data. This yields \(^{10}\) for the stress tensor

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

where \(1\) denotes the \(3 \times 3\)-unit matrix and the stress relaxation function is given by

\[
\chi(t) := \frac{\rho_0}{N} \text{Tr} \left[ (1 - E_0) \exp \left( -\frac{6t}{\zeta_0^2} \Gamma \right) \right].
\]

The symbol \(\text{Tr}\) in \(^{8}\) 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 \(^{11, 21}\). 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

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

One deduces immediately from \(^{8}\) that

\[
\Psi_2 = 0,
\]

a characteristic result for Rouse-type models. In contrast, the first normal-stress coefficient \(\Psi_1\) is non-zero

\[
\Psi_1 = \frac{1}{2} \left( \frac{\zeta_0^2}{3} \right)^2 \frac{1}{N} \text{Tr} \left( \frac{1 - E_0}{\Gamma^2} \right)
\]

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 \(\Psi_1\) of \(^{12}\) over all crosslink realisations and all crosslink strengths. To do so it is convenient to introduce the averaged density

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

of non-zero eigenvalues of \(\Gamma\). Physically, \(D\) describes the distribution of relaxation rates in the network (in units
of $\zeta a^2/6$, as is evident from the representation
\begin{equation}
\overline{\chi}(t) = \rho_0 \int_0^\infty d\gamma \exp\left\{ -\frac{6t\gamma}{\zeta a^2} \right\} D(\gamma)
\end{equation}
of the disorder average of the stress relaxation function \( \chi \). Various properties of the eigenvalue density \( D \) are discussed in detail in \[\text{[24]}\]. The average \( \overline{\chi} \) now appears as the second inverse moment of \( D \),
\begin{equation}
\overline{\chi}_1 = \frac{1}{2} \left( \frac{\zeta a^2}{3} \right)^2 \int_0^\infty d\gamma \frac{D(\gamma)}{\gamma^2},
\end{equation}
while the disorder-averaged static shear viscosity $\overline{\eta} := \overline{\sigma}_{xy}/(\rho_0 \kappa)$ is determined \( \overline{\chi}_1 \) by the first inverse moment
\begin{equation}
\overline{\eta} = \frac{1}{p_0} \int_0^\infty dt \overline{\chi}(t) = \frac{\zeta a^2}{6} \int_0^\infty d\gamma \frac{D(\gamma)}{\gamma}.
\end{equation}
At this point one can already see that \( \overline{\chi}_1 \) serves as a sensitive indicator for the gelation transition. Indeed, the Jensen inequality \[\text{[33]}\] implies
\begin{equation}
\overline{\chi}_1 \geq \frac{2 \overline{\eta}^2}{\int_0^\infty d\gamma D(\gamma)} \geq 2 \overline{\eta}^2,
\end{equation}
and hence
\begin{equation}
\ell \geq 2k
\end{equation}
with \( \ell \), respectively \( k \), denoting the critical exponent of \( \overline{\eta}_1 \) for the two different types of crosslink 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. \( \text{(38)} \) of \[\text{[24]}\] with the help of a replica approach. This gives rise to the exact result
\begin{equation}
\overline{\chi}_1 = \frac{1}{2} \left( \frac{\zeta a^2}{3} \right)^2 c \left[ -\frac{3c(1-2c)^3}{240} P_2 ^2 - \frac{4c^2-3c-1}{24c(1-2c)^2} P_2 + \frac{5P_2 - 4P_2^2}{240c^2} \ln(1-2c) \right],
\end{equation}
which is valid for all $0 < c < c_{\text{crit}} = \frac{1}{2}$. The inverse moments $P_n$ were defined in \[\text{[24]}\]. From \[\text{(19)}\] we read off the critical divergence
\begin{equation}
\overline{\chi}_1 \sim \left( \frac{\zeta a^2}{3} \right)^2 c \frac{P_2 ^2}{240} \varepsilon^{-3}, \quad \varepsilon := c_{\text{crit}} - c \downarrow 0
\end{equation}
at the gelation transition, and hence the critical exponent
\begin{equation}
\ell = 3.
\end{equation}
For $c \to 0$ one expands
\begin{equation}
\overline{\chi}_1 = \left( \frac{\zeta a^2}{3} \right)^2 \frac{P_2}{8} c + \mathcal{O}(c^2).
\end{equation}
Fig. \[2\] displays \( \overline{\chi}_1 \) 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 crosslink 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 crosslink ensemble in the next section, which has been successfully used \[\text{[34]}\] to explain static properties of polymer systems.

V. THREE-DIMENSIONAL BOND PERCOLATION

For this ensemble of crosslinks the second inverse moment 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
\begin{equation}
D_\varepsilon(\gamma) \sim \gamma^{\Delta-1} f(\gamma^*(\varepsilon)/\gamma)
\end{equation}
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 non-zero constant for $x \to 0$ and decays faster than any inverse polynomial for $x \to \infty$. In particular, this gives the power-law behaviour $D_{\varepsilon=0}(\gamma) \sim \gamma^{\Delta-1}$ asymptotically for $\gamma \to 0$ at criticality, in agreement with experiments \[\text{[25]}\]. The measured exponent values, however, scatter considerably, $\Delta \approx 0.4 \ldots 0.8$, and seem to depend on the mass of the crosslinked molecules \[\text{[27]}\]. 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 contradic-
to decay like a stretched exponential in order to accommodate the critical point. Precisely at the critical point one finds an algebraic long-time decay $\chi(t) \sim t^{-\Delta}$. Dynamical scaling relates $\Delta$ to $z$ and to the exponent $k$ of the shear viscosity

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

(25)

see e.g. [24, 37]. For $x \to 0$ the scaling function $g(x) \sim x^{-\Delta}$ to decay like a stretched exponential in order to accommodate the experimentally found Kohlrausch decay

$$\chi(t) \sim \exp\{-[t/\tau^*(\varepsilon)]^{\alpha}\}$$

(26)

of the stress-relaxation function in the sol phase away from criticality, where $\alpha$ is a non-critical and possibly non-universal exponent. We will return to (26) in the next section.

From (13), (23) and (25) we deduce $\chi_1(t) \sim \varepsilon^{-k}$ for $\varepsilon \downarrow 0$ with an exponent given by the scaling relation

$$\ell = k + z = k \frac{2 - \Delta}{1 - \Delta}.$$

(27)

Since $\Delta > 0$, we have $z > k$ and the scaling relation (27) is compatible with the inequality (18). Eq. (27) was obtained previously in [39] from a model density of relaxation times with a sharp upper cut-off.

According to (1) the viscosity exponent for the Rouse-type model under consideration is given by $k \approx 0.71$, when using three-dimensional bond percolation to generate the crosslink ensemble. Concerning $\Delta$, we are only aware of [24], 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 $k$, we suspect the numerical accuracy of the result to be rather poor. Yet, using these values, Eq. (27) predicts

$$\ell \approx 4.9$$

(28)

for the exponent of the first normal-stress coefficient $\chi_1$. 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 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 $k = 0$ [10], $z = 3$ and $\Delta = 1$ [24], and thus (27) gives $\ell = 3$ in accordance with (21).

VI. TIME-DEPENDENT NORMAL-STRESS RESPONSE

First, let us focus on the normal-stress response to the inception of a steady shear flow $\varepsilon(t) = \kappa_0 \Theta(t)$. Here $\Theta$ denotes the Heaviside-unit-step function. For each realisation of the crosslinks Eq. (3) leads to

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

(29)

in accordance with the principle of frame invariance [11]. Eqs. (3) and (12) then imply that for all crosslink concentrations below $c_{crit}$ the first normal-stress difference increases towards its steady-state value like a stretched exponential

$$\chi(t) = \kappa_0 \Theta(t) - 2 \kappa_0^2 \int_0^t dt' \chi(t')$$

(30)

with the same exponent $\alpha$ as the shear-relaxation function (29). In contrast, for $c > c_{crit}$ we deduce from (24) the algebraic growth $\chi(t) \sim t^{2-\Delta}$ for long times, a result already known on a more phenomenological basis [37].

Second, we consider a sudden shearing displacement $\varepsilon(t) = E \delta(t)$, where $\delta$ denotes the Dirac-delta function. From (3) we infer

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

(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 \([13]\) 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. \([34]\) in \([1]\), holds for each crosslink realisation 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 \([14]\) to be valid for class I simple fluids.

VII. OUTLOOK

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

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