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Stress relaxation in polymer networks: Equilibrium behavior and dynamics

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The elastic and relaxational properties of a polymer network have been calculated using a stress based formulation based on the Rouse mode expansion [W. L. Vandoolaeghe and E. M. Terentjev, *J. Chem. Phys.* **123**, 34902 (2005)]. In this article, we propose an improved Rouse mode expansion incorporating appropriate boundary conditions. In contrast to the previous work, this improved formulation provides a smooth crossover from the classical equilibrium result of rubber elasticity to the shorter-time-scale Rouse relaxation of a polymer melt. Our results are compared with the classical phantom network approach in equilibrium, as well as both equilibrium and dynamic elongation experiments. The model captures the qualitative features of the data well and some of the quantitative aspects, such as the exponents seen in the dynamic modulus $G(\omega)$. © 2007 American Institute of Physics. [DOI: 10.1063/1.2768921]

I. INTRODUCTION

The dynamics of polymer melts is well established.¹ Polymers with few entanglements are catered for by the Rouse model of relaxation, coupled with the phantom chain approximation where polymers do not “see” each other. The entangled polymers are successfully described by the tube model of Doi and Edwards, where the stress relaxation occurs via reptation out of the original tube. In large amplitude experiments convective constraint release events become increasingly important to relax the alignment of the tubes. Entanglements in the melt can be relaxed away as the chain ends are free. The situation can be contrasted with a chemically cross-linked elastomer, where polymer relaxation is hampered by permanent cross-links and proved challenging to formulate. Several theoretical attempts have been made to calculate the complex dynamic modulus in these systems² (*inter alia*). Experimentally, the dynamic modulus data have become available for a range of elastomers.^{3,4} In the regime of few entanglements, it is possible to model these elastomers as a phantom chain network, and the elastic and relaxational properties of a polymer network have been calculated using the Rouse mode expansion,^{5,6} which yielded a limited agreement with experiments. In this paper, we propose an improved Rouse mode expansion which incorporates appropriate boundary conditions for permanent chemical cross-links. As in previous works, we assume the affine deformation of cross-links without explicitly considering their thermal fluctuations. In contrast to the previous work,⁵ our improved formulation provides a smooth crossover from the traditional rubber network elasticity to the Rouse relaxation of the constituent polymer chains. We calculate the complex

dynamic modulus $G(\omega)$ of a typical network, and compare it with experiments on a “dilute” elastomer, which has few entanglements per chain. Our formulation provides an integrated model over all timescales.

II. ROUSE CHAIN PROPERTIES

Rouse chains obey the following stochastic partial differential equation:

$$\zeta \frac{\partial \mathbf{r}_n}{\partial t} = \kappa \frac{\partial^2 \mathbf{r}_n}{\partial n^2} + \hat{\mathbf{f}}_n, \quad (1)$$

where ζ is the viscous drag coefficient on each bead, κ is the spring constant, and $\hat{\mathbf{f}}_n$ is the random force due to solvent collisions with the beads. The stochastic term has the following statistical properties:

$$\langle \hat{\mathbf{f}}_n(t) \rangle = 0 \text{ and } \langle \hat{\mathbf{f}}_n(t) \hat{\mathbf{f}}_m(t') \rangle = 2\zeta k_B T \delta_{nm} \delta(t - t'). \quad (2)$$

Upon cross-linking, this chain is to be quenched into a polymer network, so the appropriate boundary conditions are those of a fixed polymer span $\mathbf{R}$ between the cross-links. Thermal cross-link fluctuations are not considered here. The boundary conditions required thus are

$$\mathbf{r}_{n=0} = 0 \text{ and } \mathbf{r}_{n=N} = \mathbf{R}. \quad (3)$$

These boundary conditions can be made homogeneous by the addition of a linear term,

$$\mathbf{r}_n(t) = n \frac{\mathbf{R}}{N} + \boldsymbol{\rho}_n(t). \quad (4)$$

The following is then obtained for $\boldsymbol{\rho}_n(t)$:

$$\zeta \frac{\partial \rho_n}{\partial t} = \kappa \frac{\partial^2 \rho_n}{\partial n^2} + \hat{\mathbf{f}}_n(t) \quad \text{with } \rho_{n=0} = 0 \text{ and } \rho_{n=N} = 0. \quad (5)$$

This is akin to the problem of ring polymers,⁷ and can be solved by employing a similar Fourier series

$$\rho_n(t) = 2 \sum_{p=1}^N \mathbf{x}_p(t) \sin\left(\frac{p\pi n}{N}\right). \quad (6)$$

This Fourier expansion clearly obeys the boundary conditions described by Eq. (5). It is similar to the standard Rouse expansion, where a cosine is used in order to respect the force-free boundary condition typically found in a polymer melt. Substituting our expansion into Eq. (5), all Fourier modes (or Rouse modes) decouple, leading to the following set of stochastic equations for each Rouse mode, $\mathbf{x}_p(t)$:

$$\zeta_p \frac{d\mathbf{x}_p}{dt} = -k_p \mathbf{x}_p + \hat{\mathbf{f}}_p, \quad (7)$$

where $\zeta_p = 2N\zeta$ is the effective drag and $k_p = 2\kappa\pi^2 p^2/N$ is the effective spring constant for the p th Rouse mode, which relaxes with the Rouse time given by $\tau_p = k_p/\zeta_p$; $\hat{\mathbf{f}}_p$ is the Fourier transform of $\hat{\mathbf{f}}_n$. Equation (7) describes the standard Itô-Wiener random processes,¹ which have the following moments:

$$\langle \mathbf{x}_p(t) \mathbf{x}_p(t) \rangle = \langle \mathbf{x}_p(0^+) \mathbf{x}_p(0^+) \rangle e^{-2t/\tau_p} + \frac{k_B T}{k_p} (1 - e^{-2t/\tau_p}) \underline{\underline{I}}, \quad (8)$$

the functional form of which is easily deduced from the δ correlations assumed, and the magnitude of which is readily obtained by imposing energy equipartition for each Rouse mode. Note the crucial role of the initial conditions. This correlation derived using Rouse dynamics will next be used to calculate the stress tensor of the elastomer.

III. ELASTOMER STRESS TENSOR

In the Rouse model, the polymeric contribution to the stress tensor is given by the following tangent correlation function:¹

$$\underline{\underline{\sigma}} = \kappa \frac{c}{N} \int_0^N dn \left\langle \frac{\partial \mathbf{r}_n}{\partial n} \frac{\partial \mathbf{r}_n}{\partial n} \right\rangle, \quad (9)$$

where c is the monomer density and the average is over the stochastic force. On substituting in the Fourier expansion of the modes for $\mathbf{r}_n$ [Eqs. (4) and (6)],

$$\underline{\underline{\sigma}} = \kappa \frac{c}{N^2} \mathbf{R} \mathbf{R}^T + \frac{c}{N} \sum_{p=1}^N k_p \langle \mathbf{x}_p(t) \mathbf{x}_p(t) \rangle. \quad (10)$$

The first term comes from the linear adjustment corresponding to the end-to-end distance of each strand; the second term follows Parseval's theorem for power spectra. When all strands are cross-linked together, a quenched average over the polymer spans at cross-linking should then be performed in the first term. Cross-linking is assumed to take place within a polymer melt without force. Therefore, the probability distribution used for this average arises from solving Eq.

(1) under the *force-free* boundary conditions appropriate for a polymer melt in equilibrium. This has the following property:

$$\langle \mathbf{R}_0 \mathbf{R}_0 \rangle = \frac{Nk_B T}{\kappa} \underline{\underline{I}}. \quad (11)$$

If this moment is used, together with the affine approximation for the deformation of a span at cross-linking, $\mathbf{R}_0$ to a current span, $\mathbf{R} : \mathbf{R} = \underline{\underline{E}} \cdot \mathbf{R}_0$, then on averaging over the Gaussian distributed $\mathbf{R}_0$,

$$\underline{\underline{\sigma}} = \frac{c}{N} \left(k_B T \underline{\underline{E}} \cdot \underline{\underline{E}}^T + \sum_{p=1}^N k_p \langle \mathbf{x}_p(t) \mathbf{x}_p(t) \rangle \right). \quad (12)$$

The dynamics of the relaxation can be calculated by making an affine approximation for the way that the modes $\mathbf{x}_p$ deform, i.e., $\mathbf{x}_p(0^+) = \underline{\underline{E}} \cdot \mathbf{x}_p(0^-)$. On substituting this back into the stress tensor and using Eq. (8), the following results:

$$\underline{\underline{\sigma}} = G_0 \underline{\underline{E}} \cdot \underline{\underline{E}}^T \left(1 + \sum_{p=1}^N e^{-2t/\tau_p} \right) + p \underline{\underline{I}}, \quad (13)$$

where $G_0 = k_B T_c/N$, and a constant p arises from the mean square stochastic term in the correlator and from the compressibility. The latter contribution to a true stress is $K(\det \underline{\underline{E}} - 1) \underline{\underline{I}}$. By assuming an isotropic contraction, it is possible to calculate the volume relaxation by setting the stress on the free surfaces to zero.⁵ We shall not require this compressibility in this analysis, as we are only dealing with shear stress. It is interesting to note that the first term within the parentheses is the classical equilibrium rubber elastic result (valid at long time scales), and the second term is identical to the dynamic stress relaxation of a polymer melt (typically relevant at shorter time scales). Our formulation combines the two time limits and provides a crossover between differing time regimes.

Typically, in classical rubber elasticity, the engineering stress is derived from the free energy as follows:

$$F = \frac{1}{2} G_0 \text{Tr}(\underline{\underline{E}} \cdot \underline{\underline{E}}^T) \rightarrow \underline{\underline{\sigma}}_E = \frac{\partial F}{\partial \underline{\underline{E}}} = G_0 \underline{\underline{E}}. \quad (14)$$

This linear engineering stress can be reconciled with the quadratic true stress of Eq. (13) by using the fact that areas transform like $\mathbf{A} = (\text{cof } \underline{\underline{E}}) \cdot \mathbf{A}_0$, where *cof* denotes the cofactor of the matrix. Using this result, we can equate the forces calculated using each stress tensor,

$$\underline{\underline{\sigma}}_E \cdot \mathbf{A}_0 = \underline{\underline{\sigma}}_T \cdot \mathbf{A} = \underline{\underline{\sigma}}_T \cdot (\text{cof } \underline{\underline{E}}) \cdot \mathbf{A}_0. \quad (15)$$

Since this is true for all areas, $\mathbf{A}_0$, it follows that $\det(\underline{\underline{E}}) \underline{\underline{\sigma}}_T = \underline{\underline{\sigma}}_E \cdot \underline{\underline{E}}^T$.

The dynamic shear modulus can be found without the need to consider further terms in the stress by considering an xy shear, γ , imposed at time 0. This leads to $x_{px}(0^+) = x_{px}(0^-) + \gamma x_{py}(0^-)$, and the stress follows from the correlations, as in Eq. (13),

$$\begin{aligned}\sigma_{xy}(t) &= \frac{\gamma_C}{N} \left(k_B T + \sum_{p=1}^N k_p \langle x_{py}(0^-) x_{py}(0^-) \rangle e^{-2t/\tau_p} \right) \\ &= G_0 \gamma \left(1 + \sum_{p=1}^N e^{-2t/\tau_p} \right),\end{aligned}\quad (16)$$

which leads to a shear modulus

$$G(t) = G_0 \left(1 + \sum_{p=1}^N e^{-2t/\tau_p} \right), \quad t > 0. \quad (17)$$

Equation (17) is our main result, and we explore its implications below.

Note that while in the classical Rouse model, N has a clear meaning of the number of segments, practically a random network has strands of different N . In classical rubber elasticity the quenched average over $\mathbf{R}_0$ eliminates the N dependence. However, the t dependent part also contains N , so polydispersity alters the dynamic modulus of the model. Since the affine approximation has been used, the impact of the length dependence is restricted. In practice the heterogeneous nature of the network would result in soft regions dominated by long N and stiffer regions dominated by shorter N .

In Ref. 5 a much more complicated expression for $G(t)$ was obtained. This expression has a much sharper transition from the rubber plateau to the crossover region between the two plateaux and has rubber ($t \rightarrow \infty$) and “glassy” ($t \rightarrow 0$) plateaux moduli that differ from the corresponding limiting values predicted by Eq. (17) by small multiplicative factors. However, in the equilibrium limit ($t \rightarrow \infty$) the model of Ref. 5 is inferior to the current model since it does not give the classical rubber elasticity result expected from any phantom chain model. This might be attributed to the way network strands were constrained with an effectively zero force on one cross-linked chain end, as discussed in more detail in Ref. 6. Moreover, the current model permits a simple, closed-form solution for describing stress relaxation in a phantom network over the whole time range.

IV. DYNAMIC SHEAR MODULUS

The dynamic shear modulus is given by the following expression:

$$G^*(\omega) = i\omega \int_{-\infty}^{\infty} dt e^{-i\omega t} G(t). \quad (18)$$

To analyze the properties of both $G^*(\omega)$ and $G(t)$ the function can be split up into the following regimes using $\tau_p = \zeta N^2 / \pi^2 \kappa p^2$. $G(t)$ can then be rewritten as follows:

FIG. 1. (a) The storage modulus, the real part of the dynamic modulus. (b) The loss modulus or the imaginary part.

$$G(t)/G_0 \approx \begin{cases} 1 + e^{-2t/\tau_1}, & t \gg \tau_1 \\ 1 + \frac{1}{2} \sqrt{\frac{\pi \tau_1}{2t}}, & t \sim \tau_1 \\ 1 + \sum_{p=1}^N e^{-2t/\tau_p}, & \tau_1 > t > \tau_p \\ N + e^{-2t/\tau_N}, & t \ll \tau_N. \end{cases}$$

The following dynamic shear moduli can be obtained from the above expressions:

$$G^*(\omega)/G_0 \approx \begin{cases} 1 + i\tau_1\omega, & \omega \ll \frac{1}{\tau_1} \\ 1 + \frac{1}{4} \pi \sqrt{\tau_1} \omega + i \frac{1}{4} \pi \sqrt{\tau_1} \omega, & \omega \sim \frac{1}{\tau_1} \\ 1 + \sum_{p=1}^N \frac{2i\omega\tau_p + (\omega\tau_p)^2}{4 + (\tau_p\omega)^2}, & \frac{1}{\tau_1} < \omega < \frac{1}{\tau_N} \\ N + 1 + i \frac{1}{\tau_N\omega}, & \omega \gg \frac{1}{\tau_N}. \end{cases}$$

In the very long time limit, $G(t) \rightarrow G_0$, Rouse relaxation is always complete, and the material returns to the rubber elastic behavior of a polymer network. In the very short time limit, no long range relaxations can take place; the spring constant between neighboring monomers are thus probed, which is N times stiffer than that of the whole polymer strand acting as a spring; hence, $G(t) \rightarrow NG_0$. Between the above two limits, as the time scale increases, more and more Rouse modes of relaxation become relevant channels for stress relaxation. Therefore, our formulation provides a smooth crossover in accounting for the dynamical behavior spanning all time scales.

From the functional forms of the dynamic modulus $G(\omega)$, it is possible to first make some schematic sketches (Fig. 1). The main features of the geometry of these curves

have been marked on the figure. These features will aid our comparison to experiment.

V. COMPARISON WITH EXPERIMENT

A. Equilibrium behavior

The equilibrium behavior ($t \rightarrow \infty$) shown by this model is the same as that of a Gaussian phantom chain network, i.e.,

$$\sigma_{zz} = G_0 \left(\lambda^2 - \frac{1}{\lambda} \right). \quad (19)$$

While several improvements to this classical expression for the true stress in a polymer network have been proposed, it is reassuring that the equilibrium behavior recovers the expected result. However, here, it is the dynamic properties that are of interest.

B. Dynamic behavior

The dynamic results are now compared to experimental results found in Ref. 4. In this paper one of the elastomers under investigation is the side-chain isotropic elastomer (SCIE). The SCIE consists of a polysiloxane backbone, with hydrocarbon side chains and difunctional hydrocarbon cross-linkers, and might be considered an isotropic analog for the nematic elastomer (which has a standard polysiloxane backbone with pendant mesogenic groups). It was estimated that a high percentage of the SCIE consists of side chains, which do not participate in the cross-linking network but act as a filler, effectively diluting the backbones. Furthermore, since the positions of the cross-linker groups along the polymer backbone are random, the SCIE can be taken to be a truly random network with a high likelihood of dangling ends and cross-link clusters. Since SCIE is dilute, entanglements are less important, enhancing the chances of a phantom model to give a reasonable fit.

The theory should provide a good fit to the data at low frequencies, so it was fitted as follows. The plateau rubber modulus G_0 and the time constant τ_1 were used to position the curve vertically and horizontally, respectively. Three values of N (the only parameter that changes the shape of the curve) are shown in Fig. 2. The lowest of these $N = 15$ corresponds to a reasonable value experimentally, and the highest of these provides an approximate fit to the glassy plateau.

As can clearly be seen from the figure, the fit to experiment for the dilute elastomer SCIE is good. The low frequency behavior produces the same exponents of 1 and 1/2, as measured experimentally.³ At higher frequencies the qualitative features of the model are consistent, but the quantitative fit becomes less convincing. This is because the details of the polymer chemistry play a more crucial role at high frequencies. Any attempt to fit a theoretical model to the data would require an unreasonable value for N since the glassy plateau obtained here is purely due to entropic constraints. At high frequencies (or very low temperatures) all polymers show a glassy behavior. In this regime the movement of chain segments is too small to be affected by cross-linking, and the monomers are effectively constrained by the

FIG. 2. The fit of the dynamic modulus to the SCIE (polysiloxane backbone) experimental data. The fitting parameters used were $\log G_0 = 4.45$, $\tau_1 = 150$ s, and three values of N shown for illustration $N = 15$, 100, and 6000.

barriers of surrounding “cages” (see, e.g., Ref. 8). The high glass modulus is thus a result of the potential forces in the process of caging, which would be included in a more detailed theory.

Furthermore, the slope of the glass transition follows a $G' \propto \omega^{0.5}$ law in theory, as is expected for a Rouse model, whereas the experimental slope is 0.6. It should be emphasized that the slope of the glass transition is, in fact, nonuniversal and system dependent.³

However, it is comforting to see that we have been successful in constructing a molecular model that accounts for the general trend, from the glassy state down to the rubbery plateau, of stress relaxation in a rubber.

VI. CONCLUSIONS

We have presented a stress based phantom chain formulation of an elastomer, which combines both the traditional rubber network elasticity and the Rouse dynamics. The result provides a smooth crossover in accounting for the dynamical behavior spanning all time scales. Our model is able to reproduce the observed scaling exponents from experiment and to provide a reasonable fit to the data at low frequencies. The high frequency behavior shows some of the same qualitative behavior. In more entangled systems the qualitatively differ-

ent behavior is not consistent with the model. Development of this model to include entanglements could result in both a better equilibrium behavior and a closer fit to the dynamics. The strength of this formulation is in its generalization to Doi and Edwards' tube formulation for entangled networks, where it offers the possibility of an analytic expression for $G(t)$.

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