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Strain-Dependent Localization, Microscopic Deformations, and Macroscopic Normal Tensions in Model Polymer Networks

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We use molecular dynamics simulations to investigate the microscopic and macroscopic response of model polymer networks to uniaxial elongations. By studying networks with strand lengths ranging from $N_s = 20$ to 200 we cover the full crossover from cross-link to entanglement dominated behavior. Our results support a recent version of the tube model which accounts for the different strain dependence of chain localization due to chemical cross-links and entanglements.

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Cross-linking a melt of linear precursor chains leads to a polymer network which macroscopically behaves as a (viscoelastic) solid and which is microscopically characterized by a complex, quenched, random connectivity and topology [1]. Over the past 60 years a large variety of theories of rubber elasticity have been put forward [2–4], and there is a corresponding body of rheological literature devoted to comparing and testing the proposed stress-strain relations, see, e.g., [5,6]. Only recently, neutron scattering experiments [7,8] and computer simulations [9–13] have begun to provide detailed microscopic information. Attempts to quantitatively correlate the microscopic and macroscopic response to strain were so far restricted to idealized model polymer networks with diamond lattice connectivity [11,12].

In this Letter we report a comprehensive set of results from computer simulations of randomly end-linked model polymer networks [10,13] under elongational strain. In our data analysis we follow the logic of most statistical mechanical theories of rubber elasticity [2,3], i.e., we relate the localization of different parts of a polymer network to strain-induced microscopic deformations and the macroscopic elastic response [4,14]. We focus on theories [1,2,15–19] based on Edwards' tube model [20], because the underlying ideas are conceptually relatively simple, (almost) completely worked out, and closely related to most modern theories of polymer rheology [14,21]. Nevertheless, a key ingredient of the model, the strain and strand length dependence of the phenomenological tube diameter, remains controversial [22,23]. Our data support a recent generalization of the tube model [15] which accounts for the different character of chain localization by cross-links [16,17] and entanglements [2,18,19].

We used extensive Molecular Dynamics (MD) simulations to study the behavior of bead-spring polymer networks under uniaxial, volume-conserving elongation. The polymer model has two interactions that represent

bonds and excluded volume, respectively. Interaction parameters are chosen to ensure conservation of the topological state. The details of the simulation methodology can be found in the literature, see, e.g., [10,13]. The present Letter is based on simulations of end-linked networks of $M \times N_s = 5000 \times 20$, 1000×35 , 2500×100 , and 3000×200 , where M denotes the number of strands and N_s the strand length. The state of the networks can be accurately characterized: the gel fraction is $>99\%$, $>91\%$ of the network is elastically active, and the fraction of four-functional cross-linkers is $>78\%$, except for 62% in the case of the 3000×200 . Each network was simulated at several elongations ($\lambda_x = \lambda_{\parallel} = \lambda$, $\lambda_y = \lambda_z = \lambda_{\perp} = 1/\sqrt{\lambda}$). The networks were successively strained. After each strain increment the networks were equilibrated, and configurations were sampled for more than 30 (2) Rouse times of the strands for the two short (long) strand networks. To reduce finite chain length effects the maximal elongations were limited to $\lambda = 2$ ($\lambda = 4$) for short (long) strand networks. Elastic properties were obtained by sampling the deviatoric part of the microscopic virial tensor defined as $\sigma_{\alpha\beta} = \langle \sum_{ij} F_{ij,\alpha} r_{ij,\beta} \rangle / V$, where the sum is over all pairs i, j of interacting beads, α, β are Cartesian indices, and F, r , and V denote forces, separations, and the volume, respectively. The normal tension is defined as $\sigma_T = \sigma_{xx} - (\sigma_{yy} + \sigma_{zz})/2$. In the following we present our simulation results together with a brief outline of the theoretical background.

With the tube model [20], Edwards proposed a tractable simplification of the complicated many-body problem of a randomly cross-linked and entangled polymer network. The key idea is that vulcanization leads to a permanent *localization* of the precursor chains (or, equivalently, long, randomly chosen paths through the network) in tubelike regions along the coarse-grained chain contours. In the following $d(\lambda_{\alpha})$ denotes the α th Cartesian component of the tube diameter, which depends only on the corresponding strain component λ_{α} , hence each elonga-

tion provides two tube diameters $d(\lambda_{\parallel})$ and $d(\lambda_{\perp})$. The zero-strain tube diameter $d(\lambda_{\alpha} = 1)$ is abbreviated d . The simplest measure of the tube diameter is the width $d_X(\lambda_{\alpha})$ of the thermal fluctuations of chemical cross-links around their average positions (Fig. 1). Our simulation runs are long enough to allow for a reliable extraction of d_X from the components of the mean-square displacements $g_{1,\alpha}(t) = \langle [r_{\alpha}(t) - r_{\alpha}(0)]^2 \rangle$, where the average is restricted to four-functional cross-links [Figs. 1(a) and 1(b)].

The key issue is the nontrivial dependence of the extracted tube diameters on strain and strand length [Figs. 1(c) and 1(d)]. From a theoretical point of view, the situation is relatively clear in the hypothetical case of “phantom networks”, which consist of noninteracting Gaussian polymer chains [24]. The corresponding tube theory by Warner and Edwards (WE) [17] uses an isotropic, strain independent tube diameter $d_{X,A}(\lambda_{\alpha}) = d_{X,A}$, where $d_{X,A} \sim b\sqrt{N_s}$ is of the order of the root-mean-square extension of the network strands. The description of polymer networks as phantom networks becomes inappropriate, if the length of the network strands approaches the melt entanglement length, N_e [14,21]. In particular, the tube diameter should become *independent* of strand length in the limit of very long strands where

$d_{X,B} \sim b\sqrt{N_e}$. The strain dependence of entanglement dominated confinement is a subtle point. Empirical evidence [8,12] and theoretical arguments [2,18,19,25] support the tube theories by Heinrich and Straube (HS) [2] and by Rubinstein and Panyukov (RP) [18] which predict an anisotropic, strain-dependent tube diameter of $d_{X,B}(\lambda_{\alpha}) = \sqrt{\lambda_{\alpha}}d_{X,B}$. HS-RP did not evaluate disorder averages over the network structure. The cross-linker contribution to the elastic properties was estimated from a phantom or constrained junction model.

The double tube theory by Mergell and Everaers (ME) [15] treats chain localization due to chemical cross-links and due to entanglements on the same level with the help of two correlated and additive confining potentials of the WE and the HS-RP type, respectively. The ME theory predicts

$$\frac{1}{d^4(\lambda_{\alpha})} = \frac{1}{d_A^4} + \frac{1}{\lambda_{\alpha}^2 d_B^4}, \quad (1)$$

with an effective zero-strain tube diameter $d^{-4} = d_A^{-4} + d_B^{-4}$. As indicated by the solid lines in Fig. 1(c), the individual data sets are well described by the functional form of Eq. (1). Moreover, the strand length dependence of the fitted cross-link and entanglement tube diameters

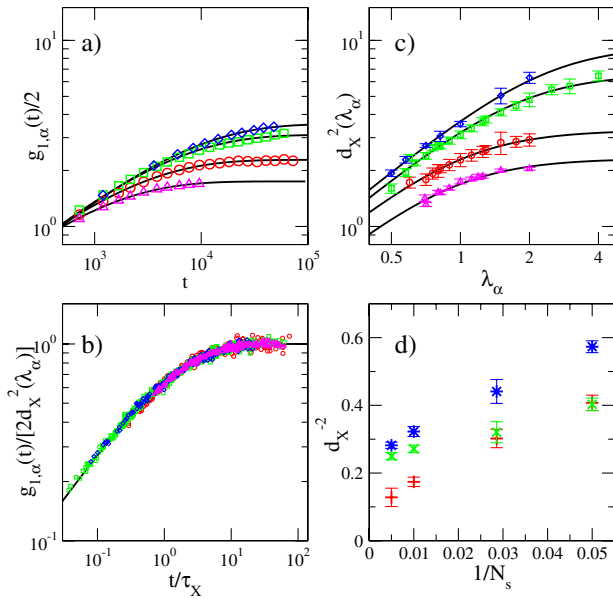


FIG. 1 (color online). Strain-dependent localization of cross-links for $N_s = 20$ (magenta \triangle), $N_s = 35$ (red \circ), $N_s = 100$ (green \square), and $N_s = 200$ (blue \diamond). (a) Cross-link mean-square displacements as a function of time for the unstrained networks. Lines are fits of $2d_X^2(\lambda_{\alpha})[1 - \exp(-\sqrt{t}/\tau_X)]$, which we use to extract the tube diameters. (b) Rescaled cross-link mean-square displacements for all $\{N_s, \lambda_{\alpha}\}$ in comparison to the fit function. (c) Strain dependence of the tube diameter. The lines are fits of Eq. (1). (d) Strand length dependence of cross-linker confinement d_X (blue *), $d_{X,A}$ component (red +), and $d_{X,B}$ component (green \times).

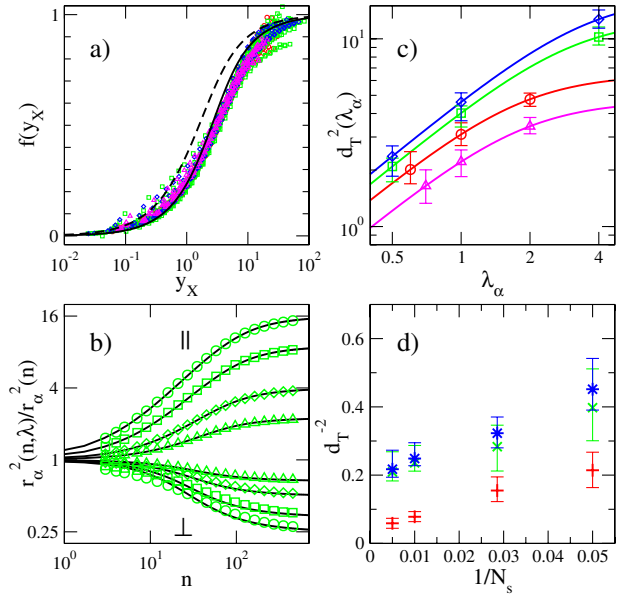


FIG. 2 (color online). Length scale dependent microscopic deformation response (symbols as in Fig. 1). (a) Scaling plot of the degree of affineness of the microscopic deformations using the tube diameters from Fig. 1(c). The lines are f_A (dashed) and f_B (solid). (b) Parallel and perpendicular microscopic deformations for the 2500×100 system for strain $\lambda = 1.5, 2, 3, 4$ (symbols). Lines are a fit of Eq. (3). (c) Strain dependence of the tube diameters. Symbols indicate the error bars and the range of λ_{α} covered by the data. (d) Strand length dependence of tube confinement d_T (blue *), $d_{T,A}$ component (red +), and $d_{T,B}$ component (green \times).

$d_{X,A}$ and $d_{X,B}$ is in good agreement with the arguments underlying the double tube theory [Fig. 1(d)]. It is worth noting that cross-links introduce additional topological constraints, hence the observed narrowing of the entanglement tube for $N_s = 20$.

In the second part of our analysis, we consider microscopic deformations. In rubberlike materials, macroscopic deformations affect distances between neighboring monomers only weakly, while distances between distant monomers change affinely with the macroscopic strain. Following the logic of the tube model, we focus on the length scale dependent deformations of nonreversal random walk paths through the network. As a probe for microscopic deformations we utilize the mean-square distances $r_\alpha^2(n, \lambda_\alpha)$ between pairs of beads as a function of their chemical distance n . In a Gaussian theory $r_\alpha^2(n, \lambda_\alpha)$ fully specifies the microscopic conformations. In the absence of strain $r_\alpha^2(n) = b^2 n$, where b^2 is one Cartesian component of the mean-square bond length for a precursor chain. End-linking is known not to change the bond length compared to the precursor melt [10]. The crossover to affine deformations can be characterized by a dimensionless function [15]

$$f = \frac{r_\alpha^2(n, \lambda_\alpha) - r_\alpha^2(n)}{(\lambda_\alpha^2 - 1)r_\alpha^2(n)}, \quad (2)$$

with $0 < f < 1$. According to the tube model the crossover length should be of the order of d_X , i.e., f should be a function of $y_X = r_\alpha^2(n)/[2d_X^2]$. Figure 2(a) verifies the interdependence of localization and microscopic deformations, which is an essential element of the tube model. Note that the plot contains *all* available data sets ($\{N_s, \lambda_\alpha\}$).

Theories based on the tube model make explicit predictions for the functional form of f [see the lines in Fig. 2(a)]: $f_A(y) = 1 + [\exp(-y) - 1]/y$ [17] and $f_B(y) = 1 + 0.5 \exp(-y) + 1.5[\exp(-y) - 1]/y$ [15] were obtained in the limits of cross-link and entanglement dominated confinement, respectively. For the general case, the double tube model [15] predicts

$$f(y) = f_A(y) + \frac{d_{T,A}^4}{d_{T,B}^4 \lambda_\alpha^2 + d_{T,A}^4} [f_B(y) - f_A(y)], \quad (3)$$

where $y = r_\alpha^2(n)/[2d_T^2(\lambda_\alpha)]$ with $d_T(\lambda_\alpha)$ given by Eq. (1).

We determined $d_{T,A}$ and $d_{T,B}$ for each system by fitting Eq. (3) to the sampled $r_\alpha^2(n, \lambda_\alpha)$ for all values of λ_α simultaneously [26]. A typical result is shown in Fig. 2(b). The effective strain-dependent tube diameters are shown in Fig. 2(c), the two components $d_{T,A/B}(N_s)$ are plotted in Fig. 2(d). As expected from the scaling plot Fig. 2(a), there is qualitative agreement between the tube diameters d_X extracted from the cross-link fluctuations and d_T inferred from the analysis of the microscopic deformations. In particular, we observe a similar crossover to entanglement dominated confinement for long strands. Not surprisingly, there is no quantitative agree-

ment between the two measures of the tube diameter. Tube models of rubber elasticity do not distinguish between middle monomers of network strands (which are free to slide along the entanglement tube) and cross-linkers (which are not) [10]. In fact, the theories discussed in this Letter employ a simple harmonic localization potential which suppresses reptationlike motion.

In the third part of our analysis we consider the macroscopic elastic response of our networks. Figure 3 shows the strain dependence of the sampled normal tensions in the form of a standard Mooney-Rivlin plot [4]. This representation is commonly used to emphasize deviations from the classical stress-strain relation $\sigma_T(\lambda) \propto (\lambda^2 - \lambda^{-1})$. Similarly to experiments [4], we find that these deviations are more pronounced for entanglement dominated systems and that the shear modulus decreases with increasing strand length.

In polymer physics [4,14] stresses are usually derived from chain conformations by dividing the chains into segments of length n . Segments are assumed to behave as independent entropic springs with spring constant $k_B T / r_\alpha^2(n)$. For a given monomer density ρ_m , the segment density is $\rho_s(n) = \rho_m / n$ [27]. Normal tensions derived from the virial tensor for this mesoscopic polymer model take a simple form involving only those ratios of mean-square internal distances which we have plotted in Fig. 2(c):

$$\sigma_{T,\text{Gauss}}(\lambda) = k_B T \lim_{n \rightarrow 0} \rho_s(n) \left[\frac{r_{\parallel}^2(n, \lambda_{\parallel})}{r_\alpha^2(n)} - \frac{r_{\perp}^2(n, \lambda_{\perp})}{r_\alpha^2(n)} \right], \quad (4)$$

There are considerable subtleties in comparing the virial tensor calculated from the full microscopic interactions to the ‘‘Gaussian’’ normal tensions [28]. Figure 3(c) shows that in the present case both quantities agree within the statistical error even though $\sigma_{T,\text{Gauss}}(\lambda) / \sigma_T(\lambda) \approx 90\%$. In

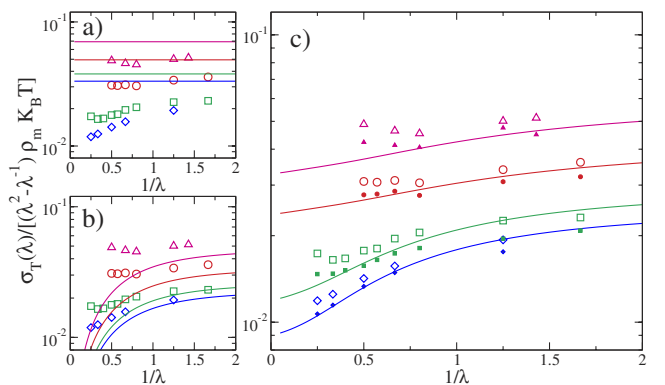


FIG. 3 (color online). Mooney-Rivlin plot of normal tensions $\sigma_T/[(\lambda^2 - \lambda^{-1})\rho_m k_B T]$ as a function of inverse strain $1/\lambda$: normal tensions sampled using the virial tensor (large symbols as in Fig. 1), and Gaussian normal tensions $\sigma_{T,\text{Gauss}}$ (small filled symbols) vs theoretical predictions based on the analysis of the microscopic deformations (Fig. 2). (a) WE cross-linker tube theory, (b) HS-RP entanglement tube theory, (c) ME theory. Symbols and lines have a 10% and 30% error, respectively.

contradiction to the arguments put forward in Ref. [9], we take the good agreement as quantitative evidence, that the tube representation of the network conformation in terms of *linear* paths through the network properly accounts for the relevant microscopic deformations.

The final step of our analysis is the *parameter-free* comparison in Fig. 3(c) of the measured stress-strain relations to the prediction of the ME theory [15]

$$\sigma_T(\lambda) = (\lambda_{\parallel}^2 - 1)g(\lambda_{\parallel}) - (\lambda_{\perp}^2 - 1)g(\lambda_{\perp}),$$

$$g(\lambda_{\alpha}) = \frac{\rho_m k_B T}{8} \frac{b^2}{d_T^2(\lambda_{\alpha})} \frac{d_{T,A}^4 + 2\lambda_{\alpha}^2 d_{T,B}^4}{d_{T,A}^4 + \lambda_{\alpha}^2 d_{T,B}^4}, \quad (5)$$

where we use the values of $d_{T,A}$ and $d_{T,B}$ from our fits of the microscopic deformations. The measured and the inferred normal tensions agree within the statistical error. To demonstrate the importance of the proper treatment of the deformation dependence of the confinement, we have also calculated stress-strain curves from the WE theory [17] ($d_T(\lambda_{\alpha}) = d_T \Leftrightarrow d_{T,B} = \infty$) and the HS-RP theory [2,18] ($d_T(\lambda_{\alpha}) = \sqrt{\lambda_{\alpha}} d_T \Leftrightarrow d_{T,A} = \infty$). The comparison in Figs. 3(a) and 3(b) shows that attempts along these lines are restricted to estimates of the order of magnitude of the elastic response.

To summarize, we have used computer simulations to determine strain-dependent localization, length scale dependent microscopic deformations, and macroscopic stresses in model polymer networks. Figure 2(a) directly validates Edward's original tube concept: on a scaling level the same length scale characterizes the spatial localization of chemical cross-links and the crossover from local liquidlike to global solidlike behavior of the microscopic chain deformations. Closer inspection [Figs. 1(c) and 2(c) and 1(d) and 2(d)] reveals the different character of (and the crossover between) cross-link and entanglement dominated confinement anticipated by the double tube model. In particular, Figs. 2 and 3 show that this model can *simultaneously* describe microscopic and macroscopic aspects of the response of our model networks to strain by accounting for the strain dependence of the (effective) tube diameter. While there remain open questions concerning longitudinal fluctuations in the entanglement tube [3,29,30], we would like to emphasize that our simulations provide a substantially improved empirical basis for addressing these and similar problems in the controlled development of statistical mechanical theories of rubber elasticity. Currently, we are analyzing the strain dependence of the primitive path mesh [31] in an attempt to systematically link the phenomenological tube model to the microscopic connectivity and topology of our model networks. Finally, we note that our simulations can also help to validate critical steps in the data analysis of (scattering) experiments addressing these issues.

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