

## New View of Entanglements in Dense Polymer Systems

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A preaveraged topological parameter,  $\tilde{N}$ , is introduced to provide a criterion for the presence of entanglements in polymer melts. The theory predicts a geometrical transition from the entangled to the unentangled state in agreement with experimental data. A generalized Rouse theory is used to describe polymer dynamics in both states.

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In the reptation model for entangled polymers,<sup>1,2</sup> a polymer diffuses in a dense network of entanglements formed by the surrounding chains. The model assumes that the entanglements are sufficiently long-lived that diffusional motion is essentially one dimensional in a confining tube. The detailed conformation of the polymer chain is replaced by a connected sequence of freely jointed links corresponding to equal-sized segments of polymer, whose length is equal to the mean number of monomers between entanglements,  $N_e$ , which then evolves in a stochastic earthworm fashion creating and destroying the tube at the ends. The phenomenological parameter  $N_e$  is assumed to be a property of the entangled chains and independent of the chain length. A direct calculation of  $N_e$ , for a particular system, has not been accomplished because of the difficulty of topological classification of entanglements. In practice,  $N_e$  is used as an experimental fitting parameter.

In this paper, we introduce a reformulation of the tube *Ansatz*. The parameter  $N_e$  is replaced by a new parameter,  $\tilde{N}$ , called the coordination number, whose value is expected to be universal. In the present theory,  $\tilde{N}$  is a geometrical property of the entangling chains and can be related to  $N_e$  and  $N_c$ , the critical chain size for the presence of long-lived entanglements. Polymer dynamics, in the entangled state, can then be described by a suitable projection of the Rouse equation onto a tube axis. Several scaling properties of polymer melts and concentrated solutions followed directly from this theory.

Our system of interest consists of Gaussian monodisperse chains with  $N$  skeletal bonds, bond length  $l$ , and bond number density  $\rho_m$ . Focusing on one chain, hereafter called the test chain, we inscribe a subsection of the chain, with  $N_e$  bonds, in a sphere of diameter  $N_e^{1/2}l$ , i.e., the mean distance spanned by the  $N_e$  bonds (see Fig. 1). For the moment  $N_e$  will be some arbitrary number less than  $N$ . In a high-density system, several other polymers will thread through this sphere and may be involved in forming entanglements with the test chain segment, or may restrict the lateral degrees of freedom of the chain. With the help of Fig. 1 we can see that the probability of this situation occurring is not independent of chain lengths. For example, if we rescale all polymer lengths

according to  $N \rightarrow N/2$  by simply cutting all polymers at their midpoints (Fig. 1, lower part), some of our scissions will occur within the test sphere. The new polymer ends produced by this cutting will lessen the probability of forming entanglements or having lateral constraints, and increase the mean spacing between entanglements accordingly.

We can quantify these arguments as follows. Let  $N(m)$  be the mean number of other polymer segments with exactly  $m$  bonds within the test sphere. Ascribing a volume  $l^3$  to each bond, we can relate the volume of the

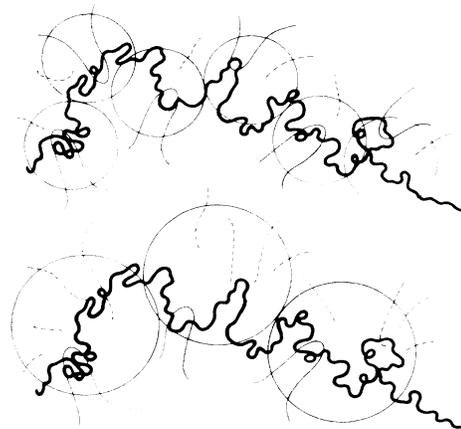


FIG. 1. Schematic illustration of the effect of polymer length on the spacing between entanglements. The heavy solid line represents a portion of the test chain. In each picture the lateral constraints are represented by the solid loops, enclosed in a sphere with diameter  $N_e^{1/2}l$ . In our model, a lateral constraint is related to the number of polymers,  $\tilde{N}$  (coordination number), of length  $O(N_e l)$ , threading through the sphere and surrounding a segment of test chain of comparable length. In the upper part, the test chain is divided into six blobs, as defined by the  $6\tilde{N}$  constraining chains. In the lower part, where the surrounding chains are shorter, the blob volume is enlarged to enclose the same number of constraining chains per blob. The dashed lines in the figure represent tail segments, which are ineffective in constraining the diffusional motion of the chain in our model. The lower part shows proportionally more tail segments enclosed in the spheres.

sphere,  $V_e$ , to  $N(m)$  by

$$\Phi V_e = l^3 \left[ N_e + \sum_{m=1}^N N(m)m \right], \quad (1)$$

where  $V_e = \pi N_e^{3/2} l^3 / 6$  and  $\Phi$  here is the polymer volume fraction. The first term on the right-hand side of Eq. (1) is due to the test segment and the second term is due to all other chain segments threading through the volume. For more general polymers, that is with bond correlations, side groups, etc., the parameter  $\Phi$  should be replaced with  $\Phi = \rho C_\infty^{3/2} l^3 / \mu_m$  where  $\rho$  is the mass density,  $\mu_m$  is the monomer molecular weight per skeletal bond, and  $C_\infty$  is the characteristic ratio.

$N(m)$  is a statistical quantity and can be computed by Monte Carlo methods.<sup>3</sup> The distribution of polymer segments, in the test sphere, can be divided into two contributions,

$$N(m) = N_{\text{tails}}(m) + N_{\text{nontails}}(m),$$

where the two terms represent the numbers of segments with tails and without tails having  $m$  bonds in the volume. With this definition, we can rewrite Eq. (1) as

$$\Phi V_e = l^3 \left[ N_e + N_e \tilde{N} + \sum_{m=1}^N N_{\text{tails}}(m)m \right], \quad (2)$$

where we introduced a parameter,  $\tilde{N}$ , called the coordination number, given by

$$\tilde{N} = N_e^{-1} \sum_{m=1}^N N_{\text{nontails}}(m)m. \quad (3)$$

Like  $N(m)$ ,  $N_{\text{tails}}(m)$  and  $N_{\text{nontails}}(m)$  can be computed directly by Monte Carlo methods.<sup>3</sup>

The physical interpretation of the coordination number is as follows. If all nontail segments, within the test sphere, have the mean length  $N_e$ , then  $\tilde{N}$  is the number of such segments in the sphere. In general, there are contributions to  $\tilde{N}$  from all lengths up to  $N$ . However, segments with  $m \ll N_e$  and  $m \gg N_e$  make a negligible contribution to the summation in Eq. (3).<sup>3</sup> Therefore, we are justified in interpreting  $\tilde{N}$  as a measure of the number of polymer segments with  $m = O(N_e)$  bonds in the volume.

The tail contribution of Eq. (2) can be computed as follows. Since the tail segments are uniformly distributed in space and the number of tails in the volume is  $\sum N_{\text{tails}}(m) = 2\rho_m V_e / N$ , we can therefore write

$$\begin{aligned} \sum_{m=1}^N N_{\text{tails}}(m)m &= \langle \text{tail} \rangle \sum_{m=1}^N N_{\text{tails}}(m) \\ &\approx \rho_m V_e N_e / N, \end{aligned} \quad (4)$$

where we have approximated the average tail length as  $\langle \text{tail} \rangle \approx N_e / 2$ . Solving Eq. (2) for  $\tilde{N}$ , we find

$$\tilde{N} + 1 = \frac{1}{6} \pi \Phi N_e^{1/2} (1 - N_e / N), \quad (5)$$

which relates the number of nontail segments,  $\tilde{N}$ , to  $N_e$ . Up until now,  $N_e$  has been an arbitrary length less than  $N$ . We now make an *Ansatz* connecting  $N_e$  with the mean spacing between entanglements or lateral constraints, by imposing a value for  $\tilde{N}$ . We will choose  $\tilde{N}$  so that, on the average, this number of neighboring nontail segments will constrain the test segment's lateral motion. These  $\tilde{N}$  segments can be either geometrical constraints or complicated knotlike entities, but their precise nature need not be specified. Once  $\tilde{N}$  is specified, then  $N_e$  can be computed, as a function of  $N$ , from Eq. (5), and interpreted as a mean constraint spacing.  $\tilde{N}$  is a preaveraged topological parameter whose value is expected to be universal.

Several results can be readily obtained from Eq. (5). For example, in the infinite-molecular-weight limit,  $N_e$  approaches a constant value

$$\lim_{N \rightarrow \infty} N_e = [6(\tilde{N} + 1) / \pi \Phi]^2. \quad (6)$$

For any finite value of  $N$ ,  $N_e$  is larger than the asymptotic limit. This is due to the increase in density of tails, which are not effective in forming constraints in our model. Figure 2 shows plots of  $N_e$  vs  $N$  for several values of  $\tilde{N}$ . Each curve terminates sharply at a value,  $N_c = 3N_e = \frac{27}{4} N_e(\infty)$ , below which the mean number of neighboring nontail polymers is less than the value required to restrict lateral motion geometrically. This transition can be understood with the help of Fig. 1. We have already argued that  $N_e$  increases as the tail density increases, i.e., with shorter chains. In order to enclose the same number,  $\tilde{N}$ , of other polymers, we must enlarge

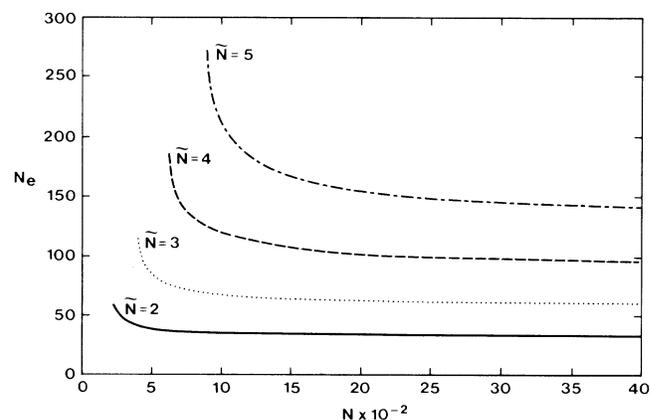


FIG. 2. The mean spacing between entanglements vs degree of polymerization for several values of the coordination number  $\tilde{N}$ . The curves approach a constant value of  $[6(\tilde{N} + 1) / \pi \Phi]^2$  for large  $N$ . Each curve terminates abruptly at a lower critical chain length  $N_c = 3^5 (\tilde{N} + 1)^2 / (\pi \Phi)^2$ . The transition to the unentangled state is geometrical in origin and is due to the increase in polymer tail density and the ineffectiveness of tail segments in forming long-lived constraints.

the sphere's diameter. As the sphere is enlarged, there is an increasing probability that we will incorporate more tails. This in turn will require that we increase the diameter of the sphere further, which rapidly becomes a self-defeating process leading to the phase transition.

Strong supporting evidence for the geometrical nature of the transition can be found in experimental diffusion and viscosity data,<sup>4</sup> where the onset of entangled behavior occurs at a value of  $N_e$  that is temperature independent. Further evidence can be found in measurements of the plateau modulus,  $G_N^0$ , in solutions where the scaling law  $G_N^0 = \rho k_B T / N_e \propto \Phi^{2.0}$  is well established experimentally<sup>4</sup> in agreement with Eq. (6).

The influence of lateral constraints on polymer dynamics can be investigated with a generalized Rouse model developed originally for polymer solutions<sup>5</sup> and applied more recently to polymer melts.<sup>6</sup> A similar approach has been used to describe rubber elasticity.<sup>7</sup> Like the original Rouse model,<sup>8</sup> the  $n$ th bond vector of the polymer chain,  $\mathbf{r}(n)$ , is decomposed into Fourier modes according to

$$\mathbf{r}(n) = 2^{1/2} N^{-1} \sum_{p=1}^N \tilde{\mathbf{r}}(p) \sin(\pi p n / N), \quad (7)$$

where  $\mathbf{r}(p)$  is given by

$$\mathbf{r}(p) = 2^{1/2} \sum_{n=1}^N \mathbf{r}(n) \sin(\pi p n / N). \quad (8)$$

The corresponding relaxation times are given by

$$\tau(p) = \alpha^2(p) \zeta N^2 l^2 / 3\pi^2 k_B T p^2, \quad (9)$$

where  $\alpha^2(p)$  is the square of the strain ratio,

$$\alpha^2(p) = \langle |\mathbf{r}(p)|^2 \rangle / \langle |\mathbf{r}(p)|^2 \rangle_0, \quad (10)$$

and  $\zeta$  is a bead-spring coefficient. The averages above are interpreted as follows:  $\langle \rangle$  represents an average over the real chain configuration and  $\langle \rangle_0$  represents an average over unperturbed chains. For a polymer melt of concentrated ideal solution,  $\alpha^2(p) = 1$ .<sup>9</sup> For entangled polymers,  $\alpha^2(p) = 1$  also holds, but the evolution of the polymer's conformation must be anisotropic in accordance with the geometrical constraints imposed by the surrounding polymers. To see this more clearly, consider the polymer chain depicted in Fig. 1. To displace the chain through a finite distance roughly along the contour of the chain conformation, one will encounter a certain amount of frictional resistance. A displacement perpendicular to the chain axis will meet with even greater resistance, if the magnitude of the displacement exceeds the spacing between entanglements. Therefore, the presence of entanglements destroys the 3D isotropy of the polymer's diffusional motion and yields nonequivalent longitudinal and transverse modes of motion.

In the framework of the Rouse theory, the interactions with other chains are purely frictional. We will there-

fore represent the effect of entanglements by defining wave-number-dependent longitudinal and transverse friction coefficients,  $\zeta_l(p)$  and  $\zeta_t(p)$ , respectively, as follows:

$$\zeta_l(p) = \zeta_0, \quad p = 1, 2, 3, \dots, N, \quad (11)$$

$$\zeta_t(p) = \begin{cases} \zeta_0, & p = \bar{p} + 1, \bar{p} + 2, \dots, N, \\ \infty, & p = 1, 2, 3, \dots, \bar{p}, \end{cases}$$

where  $\bar{p}$  is a cutoff wave number chosen to have the value  $\bar{p} = N/N_e$ . The effect of a very large, or in the present model infinite, transverse friction coefficient is to retard the lateral diffusion over length scales larger than the mean spacing between entanglements.

In order to give a formal definition to the longitudinal and transverse directions, we define a "tube" axis with a set of vectors  $\hat{\mathbf{r}}(n)$ , given by the *truncated* Fourier series

$$\hat{\mathbf{r}}(n) = 2^{1/2} N^{-1} \sum_{p=1}^{\bar{p}} \tilde{\mathbf{r}}(p) \sin(\pi p n / N). \quad (12)$$

The effect of the cutoff,  $\bar{p}$ , is to compute a weighted average over  $N/\bar{p} = N_e$  bonds around bead  $n$ . The result is a blurred image of the chain which retains the same overall conformation, but lacks the small-scale details of the chain conformation. The appropriate cutoff gives the minimum number of constraining chains, as defined earlier, required to define the tube.

We now decompose the Langevin equation for each bond into longitudinal and transverse modes by projecting each Rouse bond along the tube axis. The relaxation times of the tube modes, or equivalently the polymer longitudinal modes, are given by

$$\tau_l(p) = \langle \lambda^2(p) \rangle N \zeta_0 / 3\pi^2 k_B T p^2, \quad (13)$$

where  $\langle \lambda^2(p) \rangle / N l^2$  is the square of the strain ratio computed *along* the tube axis. After some algebra we obtain, to leading order in  $N$ ,

$$\langle \lambda^2(p) \rangle = \begin{cases} (2l^2/N_e) \cot^2(\pi p / 2N), & \text{odd } p, \\ 0, & \text{even } p. \end{cases} \quad (14)$$

Therefore, the longitudinal-mode relaxation times for odd values of  $p$  are

$$\tau_l(p) = [2l^2 \zeta_0 N / 3\pi^2 N_e k_B T p^2] \cot^2(\pi p / 2N) \quad (15)$$

which for small values of  $p$  yields  $\tau_l(p) \propto N^3 / N_e p^4$ .

The transverse relaxation times can be obtained in a similar fashion. For wave numbers  $p > \bar{p}$ , that is for diffusion of segments shorter than  $N_e$ , the test chain is not influenced by the entanglements and we have

$$\tau_t(p) = \zeta_0 l^2 N^2 / 3\pi^2 k_B T p^2. \quad (16)$$

For wave numbers  $p < \bar{p}$ , diffusion is hindered and the relaxation times are infinite in the present model. Additional nonrepetitive processes, such as the release of constraints,<sup>10</sup> would contribute to the transverse relaxation

over these length scales.

Combining Eqs. (5), (15), and (16), we have a prescription for describing polymer dynamics in both the unentangled and entangled states. Equation (5) provides a criterion for the determination of the presence of lateral constraints through a single parameter  $\tilde{N}$ . If  $N$  is less than the computed value of  $N_c$ , then the dynamics of the polymer is described by Eq. (9) and is essentially isotropic in three dimensions.

In the entangled regime,  $N > N_c$ , Eq. (5) is used to compute  $N_e$ . The longitudinal and transverse modes of relaxation are described by Eqs. (15) and (16), respectively. The value of  $N_e$  is not constant and must be computed for every value of  $N$  as depicted in Fig. 2. The  $N$  dependence of  $N_e$  in the longitudinal relaxation times modifies the scaling exponent in Eq. (15) to give an effective scaling law of the form

$$\tau_l(p) \propto N^{3+\gamma(N)}/p^4, \quad (17)$$

where the coefficient  $\gamma(N)$  varies continuously from a value of about  $\frac{1}{2}$  just above  $N_c$  and tends to zero as  $N$  is increased further. This effect will contribute to deviations from the  $\tau_l \propto N^3$  scaling law as will contour-length fluctuations<sup>11</sup> which have not been included here.

To summarize, we have presented a reformulation of the entanglement concept by making an *Ansatz* connecting lateral constraints with the presence of a certain

number of neighboring nontail segments. The parameter  $N_e$ , in the original reptation theory,<sup>1,2</sup> has been replaced by a universal topological parameter  $\tilde{N}$ . This yields predictions relating the onset of entanglements at  $N_c$  to the value of  $N_e$  and the various chain parameters. Scaling laws for concentrated solutions were then derived without additional assumptions. A generalized Rouse model and prescription for its application to entangled systems were proposed. Our approach can be generalized to other systems such as concentrated solutions in various solvents and homopolymer blends and will be presented in a future article.<sup>3</sup>

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