Predicting the Tube Diameter in Melts and Solutions

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ABSTRACT: A simple conjecture relating chain dimensions to the “tube diameter”, which represents the topological confining effect of entanglements on a chain, works well for all flexible entangled polymer melts. I extend this conjecture to semidilute solutions: first for good solvents, where it is shown to be equivalent to the Colby–Rubinstein scaling picture, and then for good solvents. In the latter case, it turns out that the number of “blobs” per entanglement strand $B$ is not a constant as had been previously assumed, but depends on the ratio of the packing length to the swelling length. This unified picture is consistent with existing data on semidilute solutions.

1. Introduction

In entangled polymer melts and solutions, the molecular weight between entanglements $\overline{M}_e$ is arguably the most fundamental material parameter, although its origin in a more microscopic description of topological constraints between chains is unclear. Two separate scaling arguments have been successfully proposed to explain the dependence of the entanglement molecular weight (and hence the tube diameter, and plateau modulus) of polymer melts on (1) polymer conformational properties (stiffness and bulkiness), and (2) polymer volume fraction in a Θ solution. This paper summarises these two arguments, due respectively to Lin and Noolandi$^{1,2}$ and others and to Colby and Rubinstein,$^{3}$ in such a way that a unified picture emerges.

A successful conjecture put forward by several authors to explain the dependence of $N_e (=\overline{M}_e\overline{M}_0, \overline{M}_0$ being the monomer mass) on the conformational properties of melt polymers can be expressed prosaically as follows: “when enough different chains get into the same room together, an entanglement happens.” This is a nontrivial statement relating $N_e$ to chain conformational properties because (1) it takes more room to bring a given number of chains together if they are flexible or bulky than if they are stiff or skinny, and (2) “enough” turns out to be the same number for all types of chains.

More precisely, the conjecture is that a fixed number $n$ of chain segments of chain length $N_e$ fit inside a volume $a^3$. This is the volume “swept out” by an entanglement segment, because the end-to-end distance of an entanglement segment is the tube diameter $a$, hence

$$a^2 = N_e b^2 \quad (1)$$

In other words, the Lin–Noolandi conjecture is

$$\frac{a^3}{N_e \Omega_0} = n \quad (2)$$

where $\Omega_0$ is the displaced volume of a monomer.

Now, recognize that the ratio $N_e \Omega_0/a^2$ is in fact a material constant, with dimensions of length and independent of $N_e$, since both numerator and denominator scale linearly with $N_e$. This length scale emerges in many contexts. For definiteness, we define the “packing length” $l_p$ as the ratio of chain displaced volume to the radius of gyration squared:

$$l_p = N\Omega_0/R_g^2(N) = 6\Omega_0/b^2 \quad (3)$$

Evidently, $l_p$ can be taken experimentally from neutron-scattering data for the radius of gyration of labeled chains of known mass in the melt (which is one reason I have chosen to use $R_g$ rather than the end-to-end radius in the definition). For the most part, $l_p$ will be used in this paper in scaling arguments, in which the numerical prefactor of eq 3 is not essential. However, section 2.4 compares numerical estimates of various length scales for various common polymers, for which the choice of prefactor matters.

Combining eqs 2 and 3, we have simply

$$a = nl_p/6 \quad (4)$$

The plateau modulus $G$ is from rubber elasticity theory generally expressible as “$kT$ per entanglement strand” or

$$G = \frac{kT}{N_e \Omega_0} \quad (5)$$

Using eqs 2–4, we find

$$G = \frac{216kT}{n^2 l_p^3} \quad (6)$$

Equations 4 and 6 are nontrivial, in that they relate an elusive property of topological origin (the tube diameter) to prosaic chain dimensions (displaced volume and end-to-end radius). Remarkably, these relations are valid for all polymers that have ever been carefully examined, with plateau moduli varying over more than 2 orders of magnitude.$^4$

Note that I have taken a different numerical prefactor in eqs 3 and 5 than were taken in ref 4. (The prefactor in eq 5 has been chosen to reflect an emerging convention in recent literature.) The correspondences between quantities in this work and ref 4 are summarized in the Appendix. With the conventions of the present paper, the experimentally determined value of $n$ is $n \approx 22.4$ or so.$^4$ Thus, $adl_p \approx 3.7$ and $G(kT/l_p^3) \approx 0.43$. 

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One interpretation of the packing length \( l_p \) is as follows: if we assume random-walk scaling of end-to-end radius with chain length \( R^2 = N b^2 \) and a volume per monomer \( \Omega_0 \), there is a length scale below which this random-walk scaling must break down or else the monomers of a single chain would overfill space. Hence ideality of chains in the melt must break down below this length scale — which is in fact \( l_p \), with corresponding chain length \( N_p \) satisfying \( N_p \Omega_0 = l_p^3 \). This length scale is larger for bulky chains (large monomeric volume \( \Omega_0 \)) or for flexible chains (small end-to-end radius \( R \)).

Bulky and/or flexible chains have a stronger tendency to fill space around a given monomer of a chain with other monomers nearby along the arclength, thus excluding monomers from other chains. We might likewise expect \( l_p \) to be the typical “distance of closest approach” of two chains, with a corresponding displaced volume of \( N_p \Omega_0 \) since two pieces of chain cannot approach more closely without overfilling space (or distorting considerably their conformations).

Thus, the Lin–Noolandi conjecture may be described as the assertion that whatever a tube is, it takes a constant number of “close approaches” between chains in a volume \( a^3 \) to define a tube segment of dimension \( a \). This number of close approaches is \( a^3 l_p^3 = (n/6)^3 \) or \( n^2/6^3 \approx 2 \) close approaches per entanglement segment.

Note that eq 3 implies that \( l_p \) for a semiflexible chain of sufficient stiffness would be smaller than the chain diameter. To see this, define \( l_b \) as the chain Kuhn length, which is \( N_b \) monomers long. On this length scale, a chain bends freely (hence subscript \( b \) for bending). The chain diameter \( d \) is then given by \( N_b \Omega_0 = l_b(\pi/4)d^2 \) (displaced volume of a Kuhn length). The chain dimensions satisfy \( R_k^2 = (NN_b) \Omega_0 h_k^2/6 \) (freely joined random walk of Kuhn lengths). Now note that the packing length can be related to \( N_b \) and \( l_b \) by \( l_p = 6N_b \Omega_0/\Omega_b^2 \), which implies \( l_p = (3\pi/2)d^2/l_b \) using the above relations.

Now for a semiflexible chain, we can have \( l_b \) increasingly larger than \( d \), so for a stiff enough chain with \( l_b > (3\pi/2)d \), we have \( l_p < d \). This is unphysical, because it is impossible for the distance of closest approach for a binary contact to be smaller than \( d \). Evidently for sufficiently stiff, skinny chains the Lin–Noolandi conjecture should be replaced by something else.

2. Extension to \( \Theta \)-Solutions

What is the proper generalization of the Lin–Noolandi conjecture to ideal but diluted entangled polymers? This question arises in multiple contexts: (1) the plateau modulus of polymer semidilute solutions in \( \Theta \) solvents; (2) the time-dependent modulus of bidisperse polymer melts on time scales between the short-chain and long-chain reptation times (assumed to be widely separated); (3) stress relaxation in star polymer melts, in which the outer portions of star arms quickly relax their stress while inner portions of star arms relax much more slowly.

The plateau modulus in \( \Theta \) solutions is related to these dynamical situations because in melts undergoing stress relaxation, the chains maintain ideal uncorrelated random-walk configurations as do the chains in \( \Theta \) solutions, even as the concentration of effectively entangling chains decreases at long time scales due to fast relaxations of some species (short chains) or portions of chains (outer portions of star arms).

2.1. Incorrect Approach. A simple (and incorrect) extension of the Lin–Noolandi conjecture that suggests itself to many people who first consider this problem is as follows: in the presence of \( \Theta \) solvent, unentangled chains, or other diluents, an entanglement volume contains some fixed number \( n \) of entanglement strands, but now at volume fraction \( \phi \) of the entangling species.

That is, \( a^3 \phi/(N_p \Omega_0) = n \).

This leads immediately to \( a(\phi) = a_0 \phi \) where \( a_0 \) is the tube diameter in the melt. Correspondingly, the concentration dependence of the entanglement chain length becomes \( N(\phi) = N_\phi \phi^2 \). The plateau modulus of “entanglement strand” in polymer solutions is given in terms of the entanglement chain length quite generally by the simple generalization of eq 5

\[
G(\phi) = \frac{k_B T \phi}{N(\phi) \Omega_0}
\]

This implies under the present assumptions \( G = G_0 \phi^3 \) where \( G_0 \) is the melt value. Unfortunately, these scaling results are in sharp disagreement with data on the concentration dependence of the modulus in \( \Theta \) solutions and dynamically diluted melts,\(^5\) which has led some workers to question the validity of the Lin–Noolandi conjecture even for melts.

It is clear upon reflection that this is not the correct extension of the Lin–Noolandi conjecture to \( \Theta \) solutions. The argument described above amounts to saying that each chain in the melt carries around a “coating” of the diluting species, in effect increasing the monomer volume from \( \Omega_0 \) to \( \Omega_0/\phi \) without changing anything else about the system. This would make sense if the diluting species were a short side branch literally attached to the polymer (and did nothing to change the end-to-end radius).

Indeed, this provides a crude approximation of the effect of short side groups in polyolefins, where the radius of gyration of the backbone is not strongly affected by the addition of side groups.\(^6\) However, the diluting species in a \( \Theta \) solution or a dynamically diluted melt are uncorrelated in position with the entangling chains, which a proper extension of the Lin–Noolandi conjecture to these situations must take into account.

2.2. Colby–Rubinstein Argument. Colby and Rubinstein formulated a correct ansatz as to the concentration dependence of the plateau modulus in \( \Theta \) solutions with the following argument,\(^3,7\) which we shall restate (in a more leisurely fashion than their original) and discuss. First, they remark that, in a \( \Theta \) solution, localized binary contacts occur randomly between portions of chains that happen to come close, and they have a volume (assumed to be independent of concentration) of \( N_p \Omega_0 \) just as in the melt. Thus, the concentration of these binary contacts is \( c(\phi) = \phi^2/(N_p \Omega_0) \), where \( \phi \) is the volume fraction of chains.

Then, they hypothesize that “some fixed (but as of yet unspecified) number of binary contacts collectively gives rise to the topological constraint which we call an entanglement”—which is the same assumption as in the Lin–Noolandi argument, extended to assume that \( n \) is independent of concentration. Thus, the tube diameter \( a(\phi) \) is assumed to scale with concentration in the same way as the near-neighbor distance between binary contacts \( l(\phi) \), where \( 1/l(\phi)^3 = c(\phi) \). If we simply take \( a(\phi) = nl(\phi)/6 \), this is the same as the Lin–Noolandi conjecture in the melt limit when \( l(\phi) \) becomes \( 6(N_p \Omega_0)^{2/3} = l_p \).
This scaling of \( a(\phi) \) proportional to \( l(\phi) \) is nontrivial, because there are several candidate “microscopic lengths” in the problem to choose from, including the correlation length for concentration fluctuations \( \xi(\phi) \), which scales differently with \( \phi \) as we shall see below. In any event, since one may write the concentration of entanglement points either as \( 1/l^2(\phi) \) or as \( \phi^2(N_c(\Omega_b)) \), Colby and Rubinstein’s assumption implies \( l(\phi) \) scales as \( (N_c(\Omega_b))^{1/2}\phi^{-2/3} \).

Thus, the tube diameter is assumed to scale as

\[
a(\phi) = a_0\phi^{-2/3}
\]

where \( a_0 \) is the melt value for the tube diameter. Because the entanglement strands are Gaussian random walks of end-to-end radius \( a \) [i.e., \( a^2 \sim N_c b^2 \)], this implies

\[
N_c(\phi) = N_c\phi^{-4/3}
\]

The corresponding result for the modulus from eq 7 is

\[
G(\phi) \sim G_0\phi^{7/3}
\]

in terms of the melt plateau modulus from eq 6. This argument is in good agreement with existing \( \Theta \) solution data of Adam and Deltsch.\(^5\)

One may then ask, how many entanglement strands of length \( N_c(\phi) \) are cohabiting a segment of tube, with volume of \( a^3(\phi) \)? Multiplying this volume by the concentration of entanglement strands \( \phi(N_c(\Omega_b)) \), we find \( \phi^{1/3}n \) strands cohabiting a tube segment. So for \( \phi \) larger than \( \phi_0 = n^{-3} = 10^{-4} \) or so, there are many entanglement strands cohabiting the same tube segment, and the theoretical picture is sensible.

2.3. What about Slip-Links? Some readers may wonder about a hypothesis for the concentration dependence of the entanglement length based on a picture of “slip-links”, which may be formulated as follows. One proposes that whatever a tube is, it consists of a sequence of localized binary entanglement events called “slip-links”, in which the motion of a given chain transverse to its own primitive path is constrained by a second chain.

Now consider a \( \Theta \) solution or equivalently a melt in which some more rapidly relaxing chains are not dynamically relevant on some longer time scale. One might be tempted to argue that if the volume fraction of entangling species is \( \phi_c \), that the probability per unit arclength of a chain of a slip-link being present should be proportional to \( \phi \).

Hence \( N_c(\phi) \) would scale as \( 1/\phi \). Correspondingly, the tube diameter would scale as \( \phi^{-1/2} \) (since \( a^2 \sim N_c \)) and the plateau modulus would scale as \( \phi^2 \) (from eq 7). Evidently, this is not the same scaling as predicted by the Colby–Rubinstein argument. Furthermore, it is ruled out by the data of ref 5. [Note that this means that the \( \phi^2 \) concentration dependence of the plateau modulus typically assumed in various formulations of stress relaxation in polydisperse linear entangled melts,\(^8\) often called “double reptation”, is not quite correct. Such theories ought to be modified to reflect the correct concentration dependence, and referred to as “seven-thirds reptation”.]

Perhaps the contrast between this unsuccessful ansatz and the successful Colby–Rubinstein hypothesis tells us something about what a tube is and is not. The successful hypothesis tells us that the number of binary contacts in a volume \( a^3(\phi) \), scaling as \( a^3(\phi)\phi^2l_p^2 \), is a constant.

The unsuccessful hypothesis would imply that the number of binary contacts of an entanglement segment of a given chain with other chains in a volume \( a^3(\phi) \) is constant. To see this, note that the concentration in the volume \( a^3(\phi) \) of a given chain’s own monomers \( \phi_{\text{self}} \) scales as \( N_c(\phi)\Omega_b a^3(\phi) \). The concentration of binary contacts between the monomers of a given chain and monomers from any chain will be proportional to the product \( \omega_{\text{self}}\phi/n^2 \) [i.e., proportional to the product of the two volume fractions, with each contact having a volume \( l_p^3 \)]. Thus, the number of contacts of the given chain with others in a volume \( a^3(\phi) \) scales as \( \phi N_c(\phi)\Omega_b l_p^3 \). If this were constant, \( N_c(\phi) \) would scale as \( 1/\phi \).

In short, the success of the Colby–Rubinstein ansatz suggests that the tube of a given chain results from binary contacts not only of the given chain with other chains, but of nearby chains with each other.

2.4. Case of \( \phi < \phi_c \). What happens for \( \phi \) less than \( \phi_c \)? Recall the scaling of the correlation length, which must equal the chain radius \( R \) at the overlap volume fraction \( \phi^* \sim N_c(\Omega_b)R^3 \), and must become independent of chain length \( N \) for concentrations well above \( \phi^* \). We thus have \( \xi(\phi) \sim R^2/\phi \), or \( \xi(\phi) = \Omega_b b^2 \phi = l_p^2 \phi \) for \( \Theta \) solutions. We may interpret \( \xi(\phi) \) as the length scale over which the monomers of a single chain passing through a region contributes a concentration that dominates the average volume fraction \( \phi \).

It turns out that \( \xi(\phi) \) and \( a(\phi) \) are comparable at \( \phi_c \), \( a(\phi) \) being larger than \( \xi(\phi) \) for \( \phi > \phi_c \). It does not make sense for \( a(\phi) \) to be smaller than \( \xi(\phi) \), because the tube is defined by other chains, and \( \xi \) is the length scale on which a single chain makes the dominant contribution to the local concentration. Hence for \( \phi < \phi_c \)–a limit difficult to achieve in practice—we must have the tube diameter given by \( \xi(\phi) \), as Colby and Rubinstein argued.

This limit is extremely hard to achieve in practice, because to obtain \( \phi^* < \phi_c \) implies a chain length \( N \) satisfying \( N > l_p^2 b \rho \phi^* \). Since \( n \) is about 20 and \( l_p/b \) is typically about unity, only enormously large chains with more than \( 10^6 \) monomers would remain overlapping below the (extremely dilute) crossover concentration \( \phi_c \).

In that hard-to-access limit, the tube diameter would be given by \( a(\phi) = l_p/\phi \) or equivalently \( a_0(n\phi) \); the entanglement length would scale as \( N_c(\phi) = l_p^2(b^2\phi^2) \), or equivalently \( N_c(\phi) = N_c(\phi)l_p^2 \). Correspondingly, the plateau modulus would scale as implied by eq 7, which is \( G_0 a_0^2\phi^3 \).

2.5. Numerical Estimates of Length Scales. At this point we make some simple numerical estimates of the various lengths we have introduced for the case of typical polymers. To begin with, the mean- square end-to-end distance of typical polymers (with carbon–carbon single bonds along the backbone) turns out to be of the order of \( 1 \text{ Å}^2 \) times the molecular weight of the backbone (in grams per mole).

In other words, to a crude first approximation, the presence of side groups along the main chain (which is essentially polyethylene) does little to affect the end-to-end distance of that backbone. (More precisely, side groups can either make the backbone more flexible, by disrupting the energy difference between trans and gauche states, or more rigid, by colliding with their neighbors along the backbone.)
This implies that the effective bond length \( b \) is approximately constant for a wide variety of polymers based on single carbon–carbon bonds, independent of the bulkiness of the polymer, with corrections arising only from changes in the Kuhn length as described above. This idea is confirmed in Table 1.

In Table 1, the values of \( R^2/M \) from which the packing length is derived [using \( l_p = 6bM/N_b(R^2) \)] come from neutron scattering measurements of \( R^2 \) in the melt [data from 4]. The values of the monomer mass \( M_b \) are on a “C\(_2\)” basis, i.e., the mass per pair of bonds along the main chain. The values for \( b \) come from \( b = (M_b R^2/M)^{1/2} \).

Evidently \( b \approx 6 \) Å for a wide range of polymers, even some with main-chain double bonds (polybutadiene [PBD] and polyisoprene [PI]) and non-carbon single bonds (polystyrene [PS] and polyvinylcyclohexane [PVC]).

We now estimate the Kuhn length \( l_b \) of a polymer (which figured in the consistency argument for the Lin–Noolandi conjecture at the end of section 1) and the corresponding number of monomers per Kuhn length \( N_b \). These are defined to satisfy \( R^2 = N_b b^2 = (N/N_b) b_0^2 \) and \( N_b l_b = l_0 \), where \( l_0 \) is the length of a monomeric step in a fully stretched chain. Thus, \( l_b = b^2/l_0 \). For polymers made of carbon–carbon single bonds, \( l_0 \) is about 2.5 Å (as above, we take a monomer to be C\(_2\) along the main chain). Hence for such polymers, \( l_b \) is about 10 Å, and \( N_b \) is about 4.

We now examine the packing length \( l_p \) for these same polymers. Using the polymer end-to-end distance as in eq 3, the values in Table 1 are obtained.\(^4\) Evidently, all these are larger than the Kuhn length (about 10 Å), with polyethylene—the skinniest polymer in the table, with the correspondingly smallest packing length—approaching \( l_p = l_b \). [Note that with the definition \( l_p = \Omega R^2(N) \) of ref 4, the values of \( l_p \) for various polymers in Table 1 would be a factor of 6 smaller, which would lead to \( l_p < l_b \) for most of the polymers in the table.]

For bulkier polymers with a carbon–carbon backbone (i.e., everything but polyethylene [PE]), we would expect that the packing length would increase as the ratio of the volume per backbone carbon to that of polyethylene (neglecting any decrease in stiffness of the backbone). This simple argument supports the observation that PE has the shortest packing length (hence smallest tube diameter, and highest plateau modulus) of any common polymer.

For chains based on stiffer backbone chemistries (e.g., multiple bonds, or biopolymers), we could certainly achieve the situation in which the packing length assuming random walk statistics turns out to be considerably smaller than the Kuhn length. For such polymers, the present picture of close binary contacts having a volume \( l_p^3 \) would not survive, since that picture is based on chains that are Gaussian or nearly so on the scale of the collision. Alternate approaches have been devised to describe entanglement for such semi-flexible chains.\(^9\)

The tube diameter for PE can be inferred directly from experimental results\(^4\) for the plateau modulus and hence the entanglement weight, which is about 1000 g/mol. This leads to a tube diameter of 30 Å or so. The important point is that this is larger than both the packing length and the Kuhn length. Hence the chain within the tube is (barely) describable as Gaussian, probably with significant corrections due to chain stiffness.

For carbon–carbon main chain polymers bulkier than polyethylene, we expect \( l_b \) to be the same or smaller, while the tube diameter will grow due to the bulk of the side groups. Thus, the description of the polymer within the tube as Gaussian should improve for polymers with side groups.

### 3. Good Solvent Regime

Finally, we turn to the case of entangled polymer solutions in a good solvent. This might be thought by most readers to be simple, with the tube diameter \( a \) scaling in the same way as the correlation length \( \xi \), as \( \xi \approx (\xi^2)^{3/4} \).

That is, the entanglement length and the correlation length are commonly thought to be proportional, with an entanglement strand consisting of a fixed number of “blobs” (correlation volumes) for all semidilute solutions, independent of concentration or polymer/solvent system.\(^10\) In the common parlance of scaling, for semidilute solutions it is often said that “there is only one length scale in the problem”, namely the correlation length \( \xi \). More precisely, this asserts that there is a scaling regime where the values of other microscopic length scales do not affect the physics and are thus “irrelevant”.

If this view were correct, it would imply that the osmotic modulus \( K \) of a semidilute solution, which scales as “\( kT \) per blob”, and the plateau modulus \( G \), which scales as “\( kT \) per entanglement strand” from rubber elasticity theory, would have a ratio \( K/G \) equal to the “number of blobs per entanglement strand” \( n_e \), independent of concentration or polymer/solvent system.\(^10\)

#### 3.1. Variation of \( K/G \)

In fact, this simplified view was shown to be incorrect by Raspau et al. and Adam.\(^11\) They examined three different polymer/good solvent systems each in the semidilute regime (PBD and PI in cyclohexane, and polystyrene [PS] in benzene), using static light scattering to measure the osmotic modulus and dynamic rheology to determine the plateau modulus.

First, Raspau et al. verified for their three systems that the osmotic modulus vs concentration obeyed a universal curve when expressed in the reduced form \( (d\Pi/dC)/(kT/M) \) vs CMA\(_2\) where MA\(_2\) is the second virial coefficient determined from light scattering. (This amounts to reducing C by the overlap concentration C\(_o\), since MA\(_2C_o^2 = \) constant) They found good agreement with the theoretically predicted power-law scaling, as had previous authors.\(^12\)

However, ref 11 concluded that while the ratio \( K/G \) was independent of concentration within experimental error, it was not the same constant for each polymer/solvent system. In fact, they found a wide range of values for the number of blobs per entanglement strand

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**Table 1. Values of Packing Length \( l_p \), Chain End-to-End Distance Per Unit Mass, Monomer Mass, and Effective Monomer Step Length \( b \)**

<table>
<thead>
<tr>
<th>polymer</th>
<th>( l_p ) (Å)</th>
<th>( R^2/M ) (Å(^2) mol/g)</th>
<th>( M_b ) (g/mol)</th>
<th>( b ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyethylene</td>
<td>10.2</td>
<td>1.25</td>
<td>28</td>
<td>5.9</td>
</tr>
<tr>
<td>polybutadiene</td>
<td>13.7</td>
<td>0.876</td>
<td>54/2</td>
<td>4.9</td>
</tr>
<tr>
<td>( a )-polypropylene</td>
<td>18.8</td>
<td>0.670</td>
<td>42</td>
<td>5.3</td>
</tr>
<tr>
<td>polyisoprene</td>
<td>19.2</td>
<td>0.625</td>
<td>68/2</td>
<td>4.6</td>
</tr>
<tr>
<td>polyisobutylene</td>
<td>20.6</td>
<td>0.570</td>
<td>56</td>
<td>5.6</td>
</tr>
<tr>
<td>polystyrene</td>
<td>23.6</td>
<td>0.434</td>
<td>104</td>
<td>6.7</td>
</tr>
<tr>
<td>poly(dimethylsiloxane)</td>
<td>24.3</td>
<td>0.457</td>
<td>78</td>
<td>6.7</td>
</tr>
<tr>
<td>poly(vinylecyclohexane)</td>
<td>33.5</td>
<td>0.323</td>
<td>110</td>
<td>6.0</td>
</tr>
</tbody>
</table>

\( a \) Note the near-constancy of \( b \) despite variation in \( l_p \).
(see Table 2). They observed that, perhaps coincidentally, the values of $K/G$ they obtained were quite close to the number of monomers in an entanglement strand in the melt (see Table 2).

The results of ref 11 invite the question of how and which other microscopic length scales affect the value of $G$ (since $K$ obeyed the expected scaling relation, the variation in $K/G$ presumably comes from $G$). In short, the complications arise from the fact that a “good solvent” does not imply that chains are self-avoiding on all length scales.

### 3.2. Scaling in Semidilute Solution

In particular, a single chain in a good solvent will only display self-avoiding behavior above a length scale $l_g$ at which the self-interaction energy is of order $kT$ (at which length scale a perturbative treatment of self-interactions breaks down13). Hence, we review the length scales that arise from considering polymer self-avoidance in semidilute solution, and then return to questions of entanglement.

In a simple mean-field, random-mixing approximation we estimate the energy of repulsive interactions $U$ per unit volume $V$ in a polymer solution of volume fraction $\phi$ by

$$U/V = w\phi^2$$  \hspace{1cm} (11)

Here $w$ is the “excluded volume parameter” that measures the strength of repulsive interactions between monomers, and hence the quality of the solvent. As $w$ approaches zero, we have a vanishing second virial coefficient between polymers and a $\Theta$ solvent; $w$ negative implies phase separation between polymer and solvent.

#### 3.3. Swelling Length

We may then ask on what length scale $l_s$ a polymer interacting with itself suffers $kT$ of repulsive energy.14 The monomer volume fraction $\phi_s$ inside the polymer coil of size $l_s$ is within random mixing approximation

$$\phi_s = \frac{N_s \Omega_0}{l_s^3} = \frac{N_p}{6l_s^3}$$  \hspace{1cm} (12)

Here $N_s$ is the number of monomers in a chain of size $l_s$, i.e., $l_s^2 = N_s \phi_s^2$.

Thus, the definition of $l_s$ above translates to

$$w\phi_s l_s^3 = kT$$  \hspace{1cm} (13)

which implies

$$\frac{l_s}{l_p} = \frac{36kT}{w\phi_s^4}$$  \hspace{1cm} (14)

The length scale $l_s$ is sometimes called the “thermal blob”; here we use the name “swelling length” to emphasize the role of $l_s$ in determining the overall chain configuration.

In a polymer solution of volume fraction $\phi$, we only expect self-avoiding behavior of the polymers at length scales between $l_s$ and the “blob size”, at which a given polymer chain begins to encounter other polymer chains so that self-avoidance is screened—roughly, there is no longer a reason to give up entropy by self-avoidance if encounters with other polymers are frequent.

To determine the blob size, we find the length scale at which the monomers from a single polymer chain contribute an average volume fraction equal to the solution volume fraction. (Thus, semidilute solution consists of blobs at overlap concentration.) Assuming the chain is self-avoiding below this length scale, the radius $\xi$ of a portion of the chain of $g > N_s$ monomers scales as

$$\xi / l_s = (g/N_s)^{2/3}$$  \hspace{1cm} (15)

In scaling parlance, each blob consists of a self-avoiding walk of “thermal blobs”, and the entire chain in semidilute solution consists of a Gaussian (not self-avoiding) walk of blobs of characteristic size $\xi$.15 This is illustrated schematically in Figure 1.

Then the volume fraction contributed by this portion of a chain is $g\Omega_0 l_s^2$, equating this to $\phi$ gives

$$\phi = \phi_s (g/N_s)^{2/3}$$  \hspace{1cm} (16)

which holds for $\phi < \phi_s$. Using the self-avoiding scaling, we have

$$\phi = \phi_s \xi^3 = (\xi / l_s)^{3/2}$$  \hspace{1cm} (17)

As the solvent quality worsens, $l_s$ increases and $\phi_s$ vanishes. At a given polymer volume fraction, as solvent quality worsens or concentration increases, eventually $\phi_s$ drops below $\phi$ and we have ideal random-walk behavior at all length scales above $l_p$.

This is the “Edwards regime”, in which mean-field theory is a valid description of the structure and interactions of a sufficiently concentrated solution of...
sufficiently weakly interacting chains. The limit of applicability of self-consistent mean-field theory is when the Edwards correlation length (which scales as \( b^2 / (\phi a)^{1/2} \)) becomes as small as the length scale at which a single chain in the solution dominates the local concentration (which scales as \( \Omega_{\text{E}}(\phi a^2) \)). Then, mean-field theory breaks down (because there are no longer a large number of chains per correlation length all interacting). The concentration at which this breakdown occurs—where the Edwards regime crosses over to a semidilute solution with swollen chains below the correlation length—is \( \phi_s \). The crossover state corresponds to thermal blobs at overlap concentration.

### 3.4. Tube Diameter

Now consider the scaling of the tube diameter. For volume fractions \( \phi \) larger than \( \phi_s \) we have in effect a \( \Theta \) solution, so the tube diameter must scale as \( a(\phi > \phi_s) = a \phi^{-2/3} \). At \( \phi_s \) we have \( a(\phi_s) = n(l_p/l_s)1/2 \phi_s \), which is to be compared to the correlation length \( \xi(\phi_s) = l_s \).

If \( \phi_s = l_p/l_s \) is greater than \( \phi_s = n^{-3} \) (true for all but the most marginal “good solvents”), the tube diameter exceeds the correlation length, which we need for consistency just as in the Colby–Rubinstein argument. [If \( \phi_s < \phi_s \), we have crossover at \( \phi_s \) to \( \phi(\phi) \) scaling as \( 1/\phi \) as for \( \Theta \) solutions.]

For \( \phi \) less than \( \phi_s \), we have self-avoidance and hence significant local correlations in the chain conformations, which invalidates the Colby–Rubinstein estimate of the concentration of “binary events” \( c_B \) proportional to \( \phi^2 \). In its place, we expect \( c_B \) to be of order one per blob volume \( \xi(\phi)^2 \).

To determine the prefactor, we force continuity at \( \phi = \phi_s \), which implies

\[
c_B(\phi < \phi_s) = \frac{l_s}{l_p \xi(\phi)^2} \tag{18}
\]

This continuity implies a connection between entanglement behavior of polymers in the melt and in the semidilute state.

With this form for \( c_B \), the same conjecture can be applied to determine the tube diameter as previously, namely \( a(\phi) = n(l_p/l_s) \) with \( 1/l(\phi)^2 = c_B(\phi) \)—the tube diameter is proportional to the distance between “binary events”—with the result

\[
a(\phi) = \begin{cases} 
  a \phi^{-2/3} & \phi > \phi_s \\
  a \phi^{-2/3}(\phi/\phi_s)^{(3-3\nu)/2} & \phi < \phi_s 
\end{cases} \tag{19}
\]

The corresponding results for the entanglement chain length \( N_e(\phi) \) and plateau modulus \( G(\phi) \) are

\[
N_e(\phi) = \begin{cases} 
  N_e \phi^{-4/3} & \phi > \phi_s \\
  N_e \phi^{-4/3}(\phi/\phi_s) & \phi < \phi_s 
\end{cases} \tag{20}
\]

\[
G(\phi) = \begin{cases} 
  G(\phi)^{7/3} & \phi > \phi_s \\
  G(\phi)^{7/3}(\phi/\phi_s)^{(3-3\nu)/2} & \phi < \phi_s 
\end{cases} \tag{21}
\]

Another way to obtain these results is to argue as follows. When two self-avoiding walks cohabit the same space, on a more local level a finite number of thermal blobs from the two chains overlap. This number is independent of the length of the walks (up to logarithmic corrections) and the solvent quality (size of the thermal blob). Physically, this is true because (1) the cost of two thermal blobs overlapping is of order \( kT \) (by definition) and (2) a few repulsive contacts of order \( kT \) between overlapping self-avoiding chains is enough to induce rearrangements of the overall chain conformations such that further contacts are avoided.

Now when two thermal blobs overlap, a mean-field description is valid, and we can estimate the number of close binary contacts of volume \( l_p^3 \) as \( l_p^3 \phi^2 l_p^3 \). Using eq 12, the number binary contacts per pair of overlapping thermal blobs scales as \( l_p/l_s \). Because there are only \( O(1) \) such overlapping thermal blobs when two self-avoiding correlation blobs of dimension \( \xi \) overlap, the concentration of binary contacts scales as \( l_p/l_s \). But this is just eq 18, from which all the scaling results including eq 22 follow.

### 3.5. What Crossover?

The values of the scaling exponents in eq 21, \( \gamma_3 = 2.33 \) and \( \gamma_4 = 2.25 \), are close enough to be indistinguishable in practice; using the best accepted value of \( \nu = 0.588 \) (see ref 17 and references therein), we have even closer values for these exponents, as \( 3\nu/(3\nu - 1) = 2.31 \).

From a purely phenomenological point of view, eq 21 asserts that the concentration dependence of the plateau modulus will be \( G(\phi) = G(\phi)^{2/3} \) all the way from the melt to overlap concentration, with no noticeable break in slope at the boundary between semidilute and Edwards regimes.

In ref 11, raw data for \( K \) and \( G \) separately are not presented. However, power-law correlations that represent their data for \( K(c) \) are reported, and a plot of values for \( K/G \) vs concentration \( c \) (in g/cm\(^3\)) is given. I have thus inferred values for \( G \) from their data, by reading off values of \( K/G(c) \) from the plot, computing \( K(c) \) from the reported power-law correlations, and taking \( G(c) = K(c)/K(0) \).

With values for melt densities \( c_0 \) and plateau moduli \( G_0 \) from ref 4, one can then make a log–log plot \( G(c)/G_0 \) vs volume fraction \( c = c/c_0 \), as shown in Figure 2. The data evidently collapses reasonably well to a single power law; the straight line has a slope of 2.3.

The prefactor of the power-law fit in Figure 2 corresponds to a melt value for \( G(c)/G_0 \) of about 0.4. One may understand this value by recalling the way in which Raspaud et al. measured the plateau modulus; namely, they defined \( G \) as the zero-shear viscosity divided by “the longest relaxation time”. This procedure will to
reasonable approximation yield 1/\(J_a\), the reciprocal of the recoverable compliance. Thus, the extrapolation to the melt should give \(G/cG_0 = 1/(J_aG_0)\).

For well-entangled polymer solutions and melts, the product \(G_0J_a\) is about 2.3.\(^{18}\) Also, there are published values for \(J_a\) for PS,\(^{19}\) PI,\(^{20}\) and PBD\(^{21}\) melts, namely \(J_a = 12, 5.9, \) and 2.0 (MPa)\(^{-1}\) respectively. Comparing to the modulus values from ref 4, we find \(G_0J_a = 2.4 \pm 0.1\) in all three cases. The prefactor in the fit of Figure 2 is in fact 1/(2.4) = 0.42.

3.6. Number of Blobs per Entanglement, \(B\). For practical purposes, the simple scaling relation \(G(\phi) = G_0\phi^{2/3}\) from melt down to overlap concentration should be adequate. Its simplicity belies the complexity of the underlying crossover from the Edwards to the semidilute regime; the exponents controlling the concentration dependence of \(G\) are close “by coincidence”.

If however we persist in answering the question posed by Raspaud et al., namely, “how many blobs comprise an entanglement strand”, we can write \(G(\phi)\) in the semidilute regime in a revealing way, as

\[
G(\phi) = \frac{kT}{n^2 \xi(\phi)^3} \left(\frac{6\lambda}{l_p}\right)^{2/3}
\]

which exposes the prefactor of the naive scaling result \(G \sim kT\lambda^{2/3}\) implied by continuity of the semidilute and Edwards regimes.

Using eq 14 we observe that the “number of blobs per entanglement” factor \(B\) can be written as

\[
B = n^2 \left(\frac{l_p}{6\lambda}\right)^{2/3} = n^2 \left(\frac{w l_p^3}{216kT}\right)^{2/3}
\]

[Note that this cannot be applied in the limit \(w \to 0\), since we must have \(l_s < \xi\) to be in the semidilute regime.]

Equation 23 shows that the number of blobs per entanglement is not a constant for all different polymer systems, but depends on the ratio of “irrelevant” microscopic lengths in the problem, \(l_p\) and \(l_s\). Qualitatively, as the repulsive interactions become stronger, \(B\) increases: more strongly self-avoiding chains have fewer chances to become entangled. Likewise, chains with a larger packing length, which are more hindered from making close approaches, have a larger value of \(B\).

4. Swelling Crossover

To check eq 23, we need the swelling length for each polymer studied. The swelling length can be obtained from the swelling dependence of chain dimensions in dilute solution.

On general grounds we expect the “swelling ratio” \(R_s/R_0\) (where \(R_0\) is the chain radius of gyration with repulsive interactions turned off) to be a function of the ratio \(R_0/l_s\). This ratio measures the importance of self-avoidance for the chain. If \(l_s > R_0\), the chain is not large enough for self-avoidance to perturb the chain dimensions very much, and the swelling ratio will tend to unity.

To describe how the swelling ratio depends on \(R_0/l_s\) we first turn to Flory theory for the swelling of a single chain.\(^{22}\) This description consists of a phenomenological free energy with three terms—chain stretching, free end entropy, and mean-field monomer–monomer interactions—in the form

\[
F = \frac{3kTR^2}{2R_0^2} - kT \log(R^2/R_0^3) + \frac{w N^2 \Omega_0^2}{2R_3}
\]

Minimizing \(F\) with respect to \(R\) yields an equation for the swelling ratio

\[
(R/R_0)^{2/3} - (R/R_0)^3 = R_d/(2l_s)
\]

which interpolates between the good-solvent scaling result \((R/R_0) = (R_0/l_s)\phi^{3/2-\epsilon}\) and the Θ-solvent result \(R/R_0 = 1\).

4.1. Swelling Curve From Simulations. In principle, the swelling curve could be computed using renormalization group techniques.\(^{23}\) An alternate approach to determining the swelling ratio as a function of \(R_0/l_s\) is to use data from Monte Carlo or molecular dynamics simulations of a self-interacting random walk. This was carried out by Graessley et al.,\(^{15}\) and compared to data on the swelling ratio as a function of chain length for a variety of polymers.\(^{24}\)

The molecular dynamics simulations of ref 17 used a bead- spring model of a polymer chain, with cutoff Lennard-Jones interactions between monomers, \(U(r) = 4\epsilon(|(12)-(12)-(6)+(12)+6\) for \(r < r_s\) (and \(U(r > r_s) = 0\)). The athermal limit was modeled by choosing the cutoff at the LJ minimum, \(r_s = 2^{1/6}\). As such the monomer interaction is purely repulsive.

To study chains with weakly repulsive interactions between monomers, the authors used a cutoff length \(r_s > 2.5\sigma\), such that the resulting interaction included most of the attractive part of the LJ interaction. Then the approach to the Θ condition is accessible by varying the simulation temperature, which was known from previous work to be \(kT_\Theta = (3.0 \pm 0.1)\epsilon.\(^{25}\)

Reference 17 showed that the radii of gyration of their chains of different lengths and temperatures fell on a master curve, when plotted as \(R_s(N, T)/R_s(N, T_\Theta)\) vs \(N/N^\ast(T)\). The scale factor \(N^\ast(T)\) was determined empirically for each temperature such that the data collapses onto a single curve, with limiting behavior for large \(N\) of the form \(R_s/R_0 = (N/N^\ast)^{-1/2}\), where \(\nu\) is the observed swelling exponent. Using this procedure, \(N^\ast = 4.03\) for the athermal chains.

In ref 24, the same approach was applied and the same collapse found for experimental data on a variety of polymer–solvent systems. The swelling crossover data for both simulations and experimental data was presented in ref 17, and is shown here as Figure 1.

The Flory result in eq 25 does not describe the crossover very well, but a phenomenological expression...
in the same spirit works quite well, namely

\[ f(R/R_0) = (R/R_0)^{5.59} - (R/R_0)^{-9.43} = (N/N^*)^{1/2} \]  

(26)

This is a “reasonable” expression [describing a somewhat sharper crossover than eq 25] in that it (1) goes to \( R/R_0 = 1 \) for small \( N \) and (2) gives \( R/R_0 = (N/N^*)^{0.089} \) for large \( N \), which is very close to the expected result \( \nu = -\frac{1}{2} \) with \( \nu = 0.588 \) the accepted value of the swelling exponent. In any event, this expression results in the solid curve in Figure 1, which represents the data very well.

4.2. Using the Swelling Crossover. With the swelling crossover curve established, experimental data on dimensions in the melt and in solution of a chain of a single molecular weight can be used to determine the swelling length in a polymer-solvent system, without varying the molecular weight to observe the crossover in that system.

Chain dimensions in solution and in the melt determine the swelling ratio \( R_g/R_0 \). From eq 26, which summarizes the crossover results of Figure 1, we can then find \( N/N^* \) as \( N/N^* = f(R_g/R_0) \), and so find \( N^* \).

To find a value for the swelling length \( l_s \), we make the definition

\[ (N/N^*)^{1/2} = R_g/l_s \]  

(27)

which may be regarded as determining the prefactor in the scaling definition of \( l_s \). [Compare eq 25 and eq 26.] The definition eq 27 makes clear that \( l_s \) is the radius of gyration of a chain of length equal to the crossover length \( N^* \), at which the chain first begins to swell.

Using eq 26, we can extract \( l_s \) as

\[ l_s = R_g/f(R_g/R_0) \]  

(28)

Data on chain dimensions in both good and \( \Theta \) solvents for several polymer systems has been tabulated by Fetters et al.\(^\text{26}\) which summarizes the data for sufficiently large molecular weights as power-law correlations with correlation coefficients above 0.99. The power laws found for the good and \( \Theta \) solvent regimes are in reasonable agreement with theoretical values for the swelling exponents.\(^\text{23}\) Chain dimension data for many polymers in the melt have also been collected\(^\text{4} \) (expressed as the coefficient \( R^2/M \) of Table 1).

From these data, we can compute values for the swelling length \( l_s \) using eq 28. In principle, we may either take \( R_g \) from chain dimensions in the melt, or in \( \Theta \) solution. For many (but not all\(^t\)) polymer systems, these are nearly the same. In Table 3, we present results for the radii of gyration, swelling ratio \( R_g/R_0 \), and swelling length \( l_s \) for several polymer systems using both melt and \( \Theta \) dimensions for \( R_g \), using data from refs 4 and 26. For these polymers, the results are evidently close.

With these results, one can compute estimates of the Edwards concentration for the three polymer systems of ref 11, using eq 12, \( \phi_{\text{ed}} = R_g/(6l_s) \). From the values of Tables 3 and 1, one finds \( \phi_{\text{ed}} = 0.24, 0.19, \) and 0.045 respectively for PS/benzene, PI/cyclohexane, and PBD/cyclohexane. Of course, eq 12 is only a scaling relation, i.e., it has implicitly an unknown coefficient of order unity. Still, the present results suggest that accessing the Edwards regime should be easier in PBD/cyclohexane than in the other two systems.

### Table 3. Chain Dimensions in Good Solvents\(^26\) and in the Melt\(^4\) and the Resulting Swelling Ratios and Swelling Lengths for Four Polymer Solvent Systems

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>( R_g \times 10^2 ) (nm)</th>
<th>( R_0 ) at ( 5 \times 10^5 \text{ g/mol} )</th>
<th>Swell Ratio</th>
<th>( l_s ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBD</td>
<td>cyclohexane</td>
<td>1.29M(^0.609)</td>
<td>14.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>dioxane (( \Theta ))</td>
<td>3.79M(^{1/2})</td>
<td>12.0</td>
<td>1.97</td>
<td>47.8</td>
</tr>
<tr>
<td></td>
<td>melt</td>
<td>3.82M(^{1/2})</td>
<td>12.1</td>
<td>1.18</td>
<td>50.8</td>
</tr>
<tr>
<td>PI</td>
<td>cyclohexane</td>
<td>1.26M(^{0.611})</td>
<td>14.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>dioxane (( \Theta ))</td>
<td>3.3M(^{1/2})</td>
<td>10.4</td>
<td>1.35</td>
<td>19.3</td>
</tr>
<tr>
<td></td>
<td>melt</td>
<td>3.23M(^{1/2})</td>
<td>10.2</td>
<td>1.38</td>
<td>16.7</td>
</tr>
<tr>
<td>PIB</td>
<td>cyclohexane</td>
<td>1.37M(^{0.595})</td>
<td>12.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>isooamylosevalerate (( \Theta ))</td>
<td>3.0M(^{1/2})</td>
<td>9.49</td>
<td>1.36</td>
<td>16.9</td>
</tr>
<tr>
<td></td>
<td>melt</td>
<td>3.1M(^{1/2})</td>
<td>9.74</td>
<td>1.33</td>
<td>20.2</td>
</tr>
<tr>
<td>PS</td>
<td>benzene</td>
<td>1.21M(^{0.595})</td>
<td>11.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cyclohexane (( \Theta ))</td>
<td>2.79M(^{1/2})</td>
<td>8.82</td>
<td>1.29</td>
<td>21.3</td>
</tr>
<tr>
<td></td>
<td>melt</td>
<td>2.69M(^{1/2})</td>
<td>8.51</td>
<td>1.34</td>
<td>16.6</td>
</tr>
</tbody>
</table>

### Table 4. Swelling-Derived Values of Excluded Volume Parameter \( w \) for Four Polymer–Solvent Systems

<table>
<thead>
<tr>
<th>System</th>
<th>( \rho ) (g/cm(^3))</th>
<th>( \Omega_0 ) (Å(^3))</th>
<th>( w\Omega_0/kT )</th>
<th>( N^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBD/cyclohexane</td>
<td>0.826</td>
<td>54</td>
<td>0.21</td>
<td>657</td>
</tr>
<tr>
<td>PI/cyclohexane</td>
<td>0.830</td>
<td>68</td>
<td>0.40</td>
<td>79</td>
</tr>
<tr>
<td>PIB/cyclohexane</td>
<td>0.849</td>
<td>109</td>
<td>0.47</td>
<td>77</td>
</tr>
<tr>
<td>PS/benzene</td>
<td>0.969</td>
<td>178</td>
<td>0.68</td>
<td>36</td>
</tr>
</tbody>
</table>

**Likewise, with the swelling length in hand one can compute a swelling-based value for the excluded-volume parameter, using eq 14 and the data of Tables 3 and 1. The results are shown in Table 4 below, where \( w \) is presented in the form \( w\Omega_0/kT \) [which equals \( 36\Omega_0/(l_s^2) \) from eq 14]. Here \( \Omega_0 = M_0/(NAP) \) the volume of a “monomer” (defined here as the volume associated with a pair of carbon atoms along the main chain).

Note that in each case \( w\Omega_0 \) is small compared to \( kT \), which means that excluded volume effects are weak in these polymer systems on a per-monomer basis. Also reported in Table 4 are the inferred values of \( N^* \) (in terms of number of monomers) for these four polymer systems. Note the relatively large value of \( N^* \) for the PBD/cyclohexane system, which likewise has the smallest value of \( w\Omega_0/kT \) and the largest value of \( l_s \) (see Table 3).

4.3. Predicting \( B \). Using the packing and swelling lengths for the polymers studied by Raspadu et al. we can compare eq 23 for the number of blobs per entanglement \( B \) with the results of ref 11. (Here I have used the swelling lengths derived from chain dimensions in the melt.) The results of this comparison (using the value \( n = 20\sqrt{5}/4 \approx 22.4 \)) are shown in Table 5. The results are quite encouraging, particularly in that this value of \( n \) that describes melt entanglement works here as well, with only a constant factor of 0.66.

In the above, the error bars on the predicted values of \( B \) are derived only from the uncertainty in the crossover curve derived from simulations, and do not reflect the additional uncertainties that arise from the experimental inputs (measured chain radii in melt and solution).

Note that the predicted value of \( K/G \) depends not only on melt properties (via \( l_p \)) but also on solvent quality as well (via \( l_s \)). The surmise of ref 11 was that...
\[ K_G = M/\rho_0 \]

only depends on melt properties, and thus cannot explain a decrease in \( K_G \) as solvent quality decreases. It would therefore be interesting to measure \( K_G \) as a function of temperature in a single polymer/solvent system in the vicinity of the \( \Theta \) point.

4.4. Gauss Winding Number. There have been several attempts\(^{27-29}\) to relate the plateau modulus or tube diameter to quantities describing the topological constraints in an entangled polymer melt or solution. This is evidently an appealing goal, since the plateau modulus in entangled polymer systems ultimately arises from uncrossability constraints, which are topological in nature.

These efforts have so far been unsuccessful. Here, I shall show that a certain plausible quantity related to the Gauss winding numbers (GWNs) of a melt or solution of entangled ring polymers reproduces the scaling results of the present paper for the plateau modulus. Once again, an essential ingredient of the argument is the packing length.

The reason for considering ring polymers is that for a configuration of such polymers, the GWN between any two polymers is a well-defined topological quantity. Of course, an actual melt of ring polymers cannot change the state of entanglement, because of uncrossability constraints. However, we can consider a “thought ensemble” of ring polymers, but with the partition function summed over all configurations without respecting uncrossability. This ensemble ought to resemble an ensemble of long entangled polymers with respect to its configurations, while still having well-defined GWNs for any pair of polymers in a given configuration.

The GWN of two loops counts the number of times that one loop winds around the other. It can be expressed as a double line integral over the two loops:

\[ w = \frac{1}{4\pi} \int \int \frac{(\hat{r}_1 \times d\hat{r}_2)(\hat{r}_1 \times \hat{r}_2)}{|\hat{r}_1 \times \hat{r}_2|^3} \quad (29) \]

which takes on integer values \( 0, \pm 1, \pm 2, \ldots \).

In fact, a simple discrete algorithm exists for computing the GWN for loops on a cubic lattice\(^{30}\) (and by implication any smooth paths that may be discretized). The algorithm proceeds as follows. First, to avoid ambiguities arising from overlaps, one of the two loops is displaced by by one-half a lattice spacing in all three coordinate directions i.e., by \((\pm \bar{x} + \bar{y} + \bar{z})/2\). The pair of loops are then projected along each of the three coordinate axes, and the crossings of the two loops so projected are counted with a contribution \( \pm \phi \). The sign of the contribution is positive (negative) if the tangent of the upper curve in the crossing must be rotated clockwise (counterclockwise) to coincide with the tangent of the lower curve. The sum of the contributions gives the GWN.

For two overlapping Gaussian random loops, it has been argued by des Cloizeaux\(^{31}\) and shown by on-lattice Monte Carlo simulation\(^{32}\) that the mean-square GWN scales as \( N^{1/2} \). The argument of des Cloizeaux amounts to saying the following: (1) the contributions to the GWN come from close approaches of the two loops; (2) the number of close approaches of two overlapping ideal random walks scales as \( N^2/R^3 \) or \( N^{1/2} \); (3) the contributions are random in sign, so the variance scales as \( N^{1/2} \) by the central limit theorem.

Of course, for two such Gaussian random loops, there are no packing constraints operating to restrict the number of close approaches. Now consider two ring polymers in a \( \Theta \) solution or melt, cohabiting the same volume. Using the same packing arguments as in previous sections, the number of contacts \( C \) between these two polymers must scale as \( \phi^2R^2l_p^3 \), where \( \phi \) refers to the volume fraction of monomers from the two rings in the volume they pervade. That is, \( \phi \) should scale as \( N\rho_0/R^3 \), so that \( C \) scales as \( R/l_p \). Since \( R \) scales as \( N^{1/2} \), this is the same as claim 2 of des Cloizeaux’s argument above, but with local packing constraints included.

Now estimate the number of loops \( n(\phi) \) that cohabit the same volume. At volume fraction \( \phi \), we must have \( n(\phi)N\rho_0 = R^3 \phi \), so that \( n(\phi) \) scales as \( (R/l_p)\phi \). Thus, if we sum the variances of the GWN of a given loop with all other loops, this sum scales as \( (R/l_p)^2\phi^2 \).

Then the sum of the variances of the GWN of all loops with all other loops, per unit volume, scales as \( (R/l_p)^2\phi^2/N\rho_0 \), which is \( \phi^2R^2/l_p^3 \). This quantity, we propose, scales as \( 1/\alpha^2(\phi) \)—which reproduces the results of the Colby–Rubinstein ansatz. In other words, each tube segment volume \( \alpha(\phi) \) on the average contains some constant number of winding or unwinding events between some pair of chains.

It would be worthwhile to test in off-lattice simulations of concentrated systems of ring polymers, equilibrated with respect to uncrossability, with variable stiffness so that the packing length varies, to see if the sum of the variance of the GWN of one loop with all others scales as predicted.

5. Conclusions

In this paper I have shown that the Lin–Noolandi conjecture for the entanglement molecular weight of polymers in the melt—that an entanglement results from a fixed number of polymer chains cohabiting the same volume—can be extended to solutions, under both \( \Theta \)- and good-solvent conditions. In the case of \( \Theta \) solutions, the conjecture is found to be consistent with the Colby–Rubinstein theoretical picture, which states that a fixed number of binary contacts between chains constitutes an entanglement strand.

In the case of semidilute solutions in good solvents, earlier authors had in effect assumed a proportionality between the number of correlation volumes or “blobs” in the solution and the number of entanglements, i.e., a plateau modulus that is a universal constant \( 1/R \) as simple scaling arguments would suggest. However, they find that the number of blobs per entanglement strand \( K_G \) is a constant for each system studied, but differs by as much as a factor of 5 from one polymer–solvent system to another.

In the present work, I construct a unified phenomenological description of counting entanglements that encompasses melts, \( \Theta \) solutions, and good-solvent conditions. As a consequence of nearly equal scaling exponents in the \( \Theta \)-solvent and good-solvent regimes, the concentration dependence of the plateau modulus is well.
described phenomenologically by \( G(\phi) = G_0 \alpha^{3-2} \) from the melt all the way down to the overlap concentration. This apparent simplicity belies the complexity of the crossover from the Edwards regime (high-concentration, mean-field behavior) to the good-solvent regime.

This unified description implies that the number of entanglements per blob \( B \) must depend on the ratio of two microscopic lengths, the packing length \( l_p \) and the swelling length \( l_s \), as \((l_p/l_s)^{23,5}\). The swelling length determines the length scale on which repulsive interactions between monomers in solution first lead to significant distortion of chain conformations, and the packing length likewise determines the length scale on which incompressibility necessitates deviations from random-walk statistics in the melt. Together, the two length scales provide a way of quantifying the effects of monomer interactions, chain stiffness, and bulkiness.

As solvent quality is reduced (monomer repulsions weakened), the swelling length increases; at any given concentration, \( l_s \) eventually reaches the blob size \( \xi \), which brings the system from the semifluid good-solvent regime to the \( \Theta \)-solvent regime. The existence of this continuous crossover requires that the entanglement density under semifluid good-solvent conditions depend on the packing and swelling lengths, since the entanglement density under \( \Theta \) conditions depends on the packing length and the location of the crossover depends on the swelling length.

The dependence of \( B \) on \( l_p/l_s \) reflects the fact that, even in the semifluid good-solvent regime, the number of close contacts between chains is affected by the physics on length scales below the swelling length. For chains that are more flexible, are more bulky, or have more strongly repulsive monomer interactions, steric hindrance and self-avoidance more effectively prevent close contacts between chains, and lead to a larger value of \( B \).

Packing lengths for real polymers can be obtained from experimental data on chain dimensions in the melt combined with melt densities and chain molecular weights. Swelling lengths for real polymers can be obtained from experimental data combined with the “swelling crossover” curve of Graessley et al.,17,24 obtained from molecular dynamics simulations of self-avoiding random walks of various lengths and repulsive interaction strengths and experimental data on various polymer-solvent systems. Essentially, one can tell from the ratio of the radius of gyration in solution to that in the melt how strongly self-avoiding is a given polymer-solvent system and thus determine the swelling length.

Given values of \( l_p \) and \( l_s \) and the present scaling theory, the number of blobs per entanglement length in good solution can be computed. Good agreement is found with the data of ref 11 for the three systems they studied. The predictions of this paper could be further tested experimentally by examining a wider range of polymer-solvent systems or by examining the temperature dependence of the osmotic and plateau moduli in a semifluid system as the \( \Theta \) temperature is approached.

Finally, I argue that local packing constraints influence the density of windings and unwindings between chains, which leads to a relation between truly topological quantities, the tube diameter, and the packing length. To study topological invariants, it makes sense to consider a “thought ensemble” of ring polymers, but with the partition function summed over all configura-