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Chain Dimensions in Amorphous Polymer Melts

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ABSTRACT: We show theoretically that the dimension of a polymer chain in the melt, as measured, for example, by the mean-square end-to-end distance or the mean-square radius of gyration, is different from that of an ideal chain, due to the local packing constraint in the melt. Although the scaling of these dimensions with the molecular weight of a polymer remains the same, the effective Kuhn length is renormalized to a larger value. The correction term is shown to be proportional to the ratio of a packing length to some microscopic cut-off length which partially reflects the effects of the local liquid structure. For an athermal binary polymer blend where the packing lengths of the two species differ, the effective Kuhn length for each polymer depends on the composition of the blend.

1. Introduction

The dimension of a polymer chain, as measured, for example, by the mean-square end-to-end distance, $\langle R^2\rangle$, or by the mean-square radius of gyration, $\langle R_g^2\rangle$, is one of the most important characteristics of polymers and can be correlated to a variety of polymer properties, such as the viscosity of a polymer solution or the plateau modulus of a polymer melt.[1]

A key concept in the study of the dimension of a polymer is that of an ideal (or unperturbed) chain.[2] In the coarse-grained, continuum representation, an ideal chain is envisaged as a noninteracting, Gaussian random walk with a persistent length (Kuhn length) b. If a polymer chain consists of N Kuhn units, then the mean-square end-to-end distance for the ideal chain is given by $\langle R^2\rangle = Nb^2$ and the radius of gyration is $\langle R_g^2\rangle = Nb^2/6$. These dimensions have been referred to as the unperturbed dimensions of a polymer chain and serve as a universal reference for discussing the dimensions of polymers in realistic situations.

The dimensions of a real polymer in solution depend on the solvent condition, such as the quality of the solvent, and the concentration of polymers in the solution.[2,3] In a good solvent, the chains are swollen, whereas in a poor solvent, the chains are collapsed. It is generally believed that in 3-dimension, to a good approximation, a polymer in a Θ solvent assumes the dimensions of the ideal chain. The unperturbed dimensions can also be realized theoretically. In particular, the rotational isomeric state (RIS) approach[2] which neglects long-range nonbonded interactions, in principle, yields the unperturbed dimensions of a polymer.

What is the dimension of a polymer in the amorphous melt state? Forty years ago, in his classical treatise,[2] Flory argued that a polymer in a melt should have the unperturbed dimension. His conclusion is based on studying the expansion coefficient α (defined as $\alpha = \langle R_g^2\rangle^{1/2}/\langle R_g^2\rangle_0^{1/2}$, where $\langle R_g^2\rangle_0$ is the unperturbed mean-square radius of gyration) in the framework of the Flory–Huggins theory for polymer solutions and mixtures. Physically, this somewhat surprising result comes about because of the screening of the excluded-volume interactions. The screening concept has been developed more systematically by Edwards for concentrated polymer solutions.[4-6]

Extensive experiments have been performed to test the Flory conjecture. X-ray,[7,8] and neutron scattering techniques[9-12] have been used to directly measure the chain dimensions of a variety of polymers in melt states. Comparisons between the chain dimension in melt and the chain dimension determined at the Θ condition appear to support Flory's conjecture. Furthermore, the theoretically calculated structure factor for labeled chains using the random-phase approximation (RPA) yields a radius of gyration for the chain in the melt that is the same as that of the unperturbed chain.[13] Thus, it is now widely accepted that a polymer in the melt has the same conformation statistics as an ideal chain.

However, in spite of the general agreement between experiments and Flory's conjecture, there are several reasons for theoretically reexamining the issue of chain dimensions in a polymer melt:

(1) A polymer at Θ condition is only approximately ideal. Although the effective two-body interactions vanish at the Θ point, residual three-body interactions lead to corrections to the ideal chain behavior.[13-17] Moreover, it has been suggested that there may be specific solvent effects that influence the local conformation of the chain at the Θ temperature for a given polymer–solvent system.[18] Thus a comparison between the chain dimension in the melt and at the Θ condition of a particular polymer–solvent system does not directly answer the question of whether a chain in the melt assumes the unperturbed dimension.

(2) While experimental data generally support the Flory conjecture, systematic deviations exist.[7,12,19] The majority of these deviations show that the size of a polymer in the melt is larger than that at the Θ condition.[20] Also, if the Flory conjecture is true, it follows that the dimension of the chain in a melt is the same as that in the unperturbed state (theoretically modeled by the rotational isomeric state (RIS) approach or experimentally approximated by the Θ condition) at all temperatures; i.e., the temperature dependence of the radius of gyration is the same for the two conditions. Comparisons between small-angle neutron scattering (SANS) measurements, on the one hand, and RIS calculations and Θ solvent based data, on the other hand, increasingly suggest otherwise.[21-24]

(3) The Flory argument was based on the Flory–Huggins mean-field theory of polymer solutions and mixtures. Recent theoretical[25-28] and experimental studies[29,30] have shown that local packing constraints and thermal fluctuations beyond the Flory–Huggins

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level can give rise to entropic corrections to the Flory–Huggins free energy of polymer blends. Therefore, theoretically it is not surprising that similar effects can also lead to changes in the chain dimension in the bulk state or blend from its unperturbed value. Indeed, it has been shown that the chain dimensions in a blend can change as a result of enthalpic interactions.[31,32] Also, McCoy et al.[33] have recently addressed some issues concerning the local correlations of polymers in the melt state, although their focus and approach are different from ours.

In this paper, we present a direct calculation of the end-to-end distance and radius of gyration of polymer chains in melt states, using a coarse-grained model. To avoid any ambiguity, we will take as the reference the dimensions of the unperturbed, ideal chain as given by $\langle R^2\rangle_0 = Nb^2$ and $\langle R_g^2\rangle_0 = Nb^2/6$ (rather than the dimensions of the polymers at Θ condition), where b is the Kuhn length of the unperturbed chain. Our calculation shows that the dimensions of polymers in melt states are always larger than the unperturbed dimensions and depend on the details of local liquid structure through a cut-off length scale λ. The expansion in the chain dimensions in the melt state is reflected in a new, effective (renormalized) Kuhn length b_R. For a single-component melt, b_R is found to be

$$b_R^2 = b^2(1 + 4l/\pi\lambda) \tag{1.1}$$

where l is the so-called packing length defined as v/b^2, with v being the volume of a Kuhn unit.[34] Notice that the parameter l is (aside from a constant numerical factor of 6) simply the inverse of the parameter β^2 introduced by Helfand and Sapse[35] which is also the natural parameter appearing in the recent work of Fredrickson et al.[28] Thus from eq 1.1, we see that the relative correction to the mean-square radius of gyration or end-to-end distance is proportional to the ratio between the packing length and the cut-off length. For an athermal binary blend (with no excess volume) with volume fractions ϕ_1 and ϕ_2 for the two polymers ($\phi_1 + \phi_2 = 1$), the effective Kuhn length for component i is given by

$$b_{iR}^2 = b_i^2\left(1 + \frac{4l_i}{\pi\lambda}\frac{l_i}{\bar{l}}\right) \tag{1.2}$$

where $\bar{l} = \phi_1 l_1 + \phi_2 l_2$ is the volume fraction averaged packing length of the blend. Thus, the effective Kuhn length of a polymer in blends, in general, depends (though weakly) on the composition.

An expression similar to eq 1.1 was derived by Edwards for the size of a polymer in moderately concentrated solutions.[5,6] For polymers with excluded-volume interaction parameter (second virial coefficient) w and concentration c, the expansion factor was shown to be

$$1 + \frac{2\sqrt{3}}{\pi}\frac{w^{1/2}}{b^3 c^{1/2}} \tag{1.3}$$

It is tempting to use the above expression for a polymer melt. Indeed, if one assumes $c \sim w^{-1}$ and takes w to be on the order of the monomer volume, one obtains an expression very similar to ours, with $\lambda = b$. However, such an extrapolation is too far-fetched. The primary effect that eq 1.3 addresses is that the chain becomes Gaussian in concentrated solutions and that the dimension of a polymer decreases with increasing concentration. It was derived assuming that the interaction is dominated by a second virial pseudopotential. The range of validity for the application of eq 1.3 is $w^2/b^6 < cw < 1$.[4,6] For polymers, this corresponds roughly to the order of 1–10% volume or weight fraction. At higher concentrations, higher order virial terms become important. The nearly uniform density in a polymer melt results from complicated interactions (both repulsive and attractive) that would involve all virial terms and is more appropriately and conveniently modeled by an incompressibility (i.e., uniform density) constraint. Although incompressibility has also been modeled in the literature by using a two-body repulsive interaction parameter, the limit is obtained by setting that parameter to be infinity, making eq 1.3 ill-defined. Thus, while eq 1.3 does show that the chain dimension in moderately concentrated solutions is different from (larger than) the ideal dimension, it cannot be used to address the packing effect on the chain dimension in an incompressible polymer melt. In principle, a lattice version of our theory can be constructed for predicting the dimension of a polymer in a lattice model of self-avoiding and mutually avoiding chains with no vacancies, a system where a second virial treatment is clearly inapplicable.

In the next section, we outline some theoretical steps that lead to eqs 1.1 and 1.2. We focus on a calculation of the mean-square end-to-end distance of chains for a single-component polymer melt. The radius of gyration can be similarly calculated; also, extension to an athermal binary polymer blend is straightforward. Therefore, we will simply mention some noteworthy points regarding these calculations while dispensing with most of the details. Our results are discussed in section 3. In particular, we address the discrepancy between our predictions and the structure factor result calculated from RPA.

2. Theory

We start with the reference system of n noninteracting, ideal (Gaussian) chains. We use the Edwards continuous representation of the polymer chains;[6] the Hamiltonian (normalized by k_BT) is

$$H_0(\mathbf{R}) = \frac{3}{2b^2}\sum_{j=1}^{n}\int_0^N ds \left[\frac{d\mathbf{R}_j(s)}{ds}\right]^2 \tag{2.1}$$

where b and N denote the Kuhn length and the number of Kuhn segments of the chains, respectively, and $\mathbf{R}_j(s)$ represents the spatial position of the sth segment on the jth chain.

The canonical configuration partition function for the n noninteracting chains can be easily evaluated as

$$Z_0 = \frac{1}{n!}\int \mathscr{D}\mathbf{R} \exp[-H_0(\mathbf{R})] = \frac{1}{n!}V^n z_0^n \tag{2.2}$$

where $\mathscr{D}\mathbf{R}$ denotes integration over the positions of all Kuhn segments of all chains in the system, V is the total volume, and z_0 is the partition function of a single ideal chain with one end fixed (at any point) in space.

In the high-density melt state, the number of configurations of the chains is greatly reduced because of the strong short-range repulsions. Following a common practice in treating polymer melts, we account for these local interactions by a local incompressibility constraint. If we define the microscopic volume fraction of the chains as

$$\phi(\mathbf{r}) = v\sum_{j=1}^{n}\int_0^N \mathrm{d}s\ \delta[\mathbf{r} - \mathbf{R}_j(s)] \qquad (2.3)$$

where $v = V/nN$ is the volume of a Kuhn unit, then the incompressibility condition is written as

$$\phi(\mathbf{r}) = 1 \qquad \text{for all } \mathbf{r} \qquad (2.4)$$

The incompressibility condition is more conveniently written in Fourier space as

$$\hat{\phi}(\mathbf{k}) = 0 \qquad \text{for } \mathbf{k} \neq 0 \qquad (2.5)$$

where the **k**th component is given by

$$\hat{\phi}(\mathbf{k}) = V^{-1}v\sum_{j=1}^{n}\int_0^N \mathrm{d}s\ \exp[i\mathbf{k}\cdot\mathbf{R}_j(s)] \qquad (2.6)$$

The $\mathbf{k} = 0$ component of $\hat{\phi}(\mathbf{k})$ is simply the overall volume fraction (which is 1 in the case of a single-component melt) and does not fluctuate in the canonical ensemble.

With the constraint eq 2.5, the configuration partition function for the melt is written as

$$Z = \frac{1}{n!}\int \mathscr{D}\mathbf{R}\ \exp[-H_0(\mathbf{R})]\prod_{\mathbf{k}>0}\delta[\hat{\phi}(\mathbf{k})] \qquad (2.7)$$

A comment on the incompressibility condition is in order. With the microscopic volume fraction defined as in eq 2.3, it is clearly impossible to have a uniform, instantaneous density at every spatial point down to arbitrarily microscopic scales. Thus, physically, eq 2.4 is to be understood as applying only beyond a certain length scale λ. Alternatively, the constraint in Fourier space (eq 2.5) is to be understood as applying only up to a momentum cutoff $2\pi/\lambda$. Therefore, a cutoff is implied in the product of δ functions inserted in the partition function eq 2.7.

In order to calculate the mean-square end-to-end distance of the chains, we introduce an auxiliary parameter η that couples to the square of the end-to-end distance vectors of all the chains in the system and define a new Hamiltonian

$$H_0(\mathbf{R};\eta) = H_0(\mathbf{R}) + \frac{3}{2b^2}\eta\sum_{j=1}^{n}[\mathbf{R}_j(N) - \mathbf{R}_j(0)]^2 \qquad (2.8)$$

Instead of eq 2.7 the partition function now becomes

$$Z(\eta) = \frac{1}{n!}\int \mathscr{D}\mathbf{R}\ \exp[-H_0(\mathbf{R};\eta)]\prod_{\mathbf{k}>0}\delta[\hat{\phi}(\mathbf{k})] \qquad (2.9)$$

so that

$$\langle R^2\rangle = \langle[\mathbf{R}(N) - \mathbf{R}(0)]^2\rangle = -\frac{2b^2}{3}n^{-1}\left[\frac{\partial \ln Z(\eta)}{\partial\eta}\right]_{\eta=0} = \frac{2b^2}{3}n^{-1}\left[\frac{\partial F(\eta)}{\partial\eta}\right]_{\eta=0} \qquad (2.10)$$

where $F(\eta) = -\ln Z(\eta)$ is the free energy (scaled by k_BT) of the melt with the Hamiltonian eq 2.8. Since only the first derivative at $\eta = 0$ is required for the calculation of $\langle R^2\rangle$, we only need to compute $F(\eta)$ to first order in η.

We note that the Hamiltonian eq 2.8 can be thought of as representing polymers with a fictitious, massless spring connecting the two ends of each chain. Moreover, the parameter η^{-1} can be thought of as the number of (fictitious) Kuhn segments that connect the two ends to the chains. Note that $\eta = 0$ corresponds to a chain with free ends, whereas $\eta = \infty$ corresponds to a ring. This analogy allows us to obtain the various statistical properties corresponding to the Hamiltonian eq 2.8 in a straightforward way.

We now proceed to calculate $Z(\eta)$. Introducing the integral representation of the δ function by a functional integral over a conjugate field ψ with Fourier components $\psi(\mathbf{k})$,[6] we can write the partition function as

$$Z(\eta) = \frac{1}{n!}\int \mathscr{D}\mathbf{R}\ \exp[-H_0(\mathbf{R};\eta)]\prod_{\mathbf{k}>0}\int\frac{\mathrm{d}\psi(\mathbf{k})}{\pi^2} \times \exp\{i\sum_{\mathbf{k}\neq 0}\hat{\phi}(\mathbf{k})\ \psi(-\mathbf{k})\} = Z_0(\eta)\prod_{\mathbf{k}>0}\int\frac{\mathrm{d}\psi(\mathbf{k})}{\pi^2} \times \exp[-nG(\psi;\eta)] \qquad (2.11)$$

where $Z_0(\eta)$ is the partition function for the noninteracting, ideal chains represented by the Hamiltonian equation (2.8). The functional $G(\psi;\eta)$ is defined by

$$G(\psi;\eta) = -\ln\langle\exp[iV^{-1}\sum_{\mathbf{k}\neq 0}\hat{\phi}^{(1)}(\mathbf{k})\ \psi(-\mathbf{k})]\rangle_{0,\eta} \qquad (2.12)$$

where $\hat{\phi}^{(1)}(\mathbf{k})$ denotes the contribution of a single chain to the total $\hat{\phi}(\mathbf{k})$, and the average is taken with respect to the single, noninteracting, Gaussian chain, with the fictitious spring coupling term.

The function $G(\psi;\eta)$ can be computed systematically to arbitrary orders as a power expansion in ψ by evaluating the multipoint correlation functions of the single chain density; interested readers may consult ref 6 for the details of the computation. In the present calculation, we make a Gaussian approximation for the functional integral by retaining terms only up to the quadratic order. Similar approximations have been used to study concentrated polymer solutions[6] and polymer blends.[28]

In the Gaussian approximation, eq 2.12 becomes

$$Z(\eta) = Z_0(\eta)\prod_{\mathbf{k}>0}\int\frac{\mathrm{d}\psi(\mathbf{k})}{\pi^2} \times \exp\left[-\frac{1}{2}V^{-1}\sum_{\mathbf{k}\neq 0}NvQ(k;\eta)\ \psi(\mathbf{k})\ \psi(-\mathbf{k})\right] \qquad (2.13)$$

where $Q(k;\eta)$ is the density–density correlation function of a single, ideal chain in the presence of the fictitious spring:

$$Q(k;\eta) = V^2v^{-2}\langle\hat{\phi}^{(1)}(\mathbf{k})\ \hat{\phi}^{(1)}(-\mathbf{k})\rangle_{0,\eta} \qquad (2.14)$$

Performing the Gaussian functional integral and taking the logarithm of eq 2.13, we find, apart from some uninteresting constant,

$$F(\eta) = \frac{V}{2(2\pi)^3}\int \mathrm{d}\mathbf{k}\ \ln[NvQ(k;\eta)] - \ln Z_0(\eta) \qquad (2.15)$$

where we have converted the sum over **k** into an integral.

The partition function $Z_0(\eta)$ can be written as

$$Z_0(\eta) = Z_0(0)\, Z_0(\eta)/Z_0(0) \qquad (2.16)$$

where $Z_0(0)$ is the partition function of the noninteracting Gaussian chains given by eq 2.1 and the argument 0 indicates the absence of the η coupling term. Exploiting the physical model as represented by the Hamiltonian eq 2.8, we can easily obtain the ratio of the two partition functions in eq 2.16; it is

$$Z_0(\eta)/Z_0(0) = (1 + \eta N)^{-3n/2} \qquad (2.17)$$

Thus,

$$-\ln Z_0(\eta) = -\ln Z_0(0) + \frac{3n}{2}\ln(1 + \eta N) = F_0(0) + \frac{3n}{2}\eta N + O(\eta^2) \qquad (2.18)$$

where $F_0(0) = -\ln Z_0(0)$ is the free energy of the noninteracting, Gaussian chains in the absence of the η coupling term.

To first order in η, the function $Q(k;\eta)$ defined by eq 2.14 can be evaluated to be

$$Q(k;\eta) = g(x) + \eta N r(x) \qquad (2.19)$$

where $x = k^2Nb^2/6$,[36] $g(x)$ is the Debye function

$$g(x) = 2x^{-2}[x + \exp(-x) - 1] \qquad (2.20)$$

and the function $r(x)$ is given by

$$r(x) = x\, \partial^2 g(x)/\partial x^2 \qquad (2.21)$$

Thus to first order in η, the free energy is

$$\Delta F(\eta) = F(\eta) - F_0(0) = \frac{V}{2(2\pi)^3}\int d\mathbf{k}\, \ln[Nvg(x)] + \frac{3}{2}n\eta N + \frac{\eta N V}{2(2\pi)^3}\int d\mathbf{k}\, \frac{r(x)}{g(x)} \qquad (2.22)$$

The mean-square end-to-end distance, from eq 2.10, is then

$$\langle R^2\rangle = \frac{2}{3}b^2 n^{-1}\left[\frac{\partial \Delta F(\eta)}{\partial \eta}\right]_{\eta=0} = Nb^2 + \frac{1}{3}b^2 n^{-1}\frac{V}{(2\pi)^3}\int d\mathbf{k}\, \frac{Nr(x)}{g(x)} = Nb^2\left[1 + \frac{1}{6\pi^2}Nv\int_0^{k_c} dk\, k^2\frac{r(x)}{g(x)}\right] \qquad (2.23)$$

where k_c is the cutoff at large k and we have made use of the fact that $V = nNv$.

To evaluate the intergral in eq 2.23, we exploit the asymptotic behaviors of the functions $g(x)$ and $r(x)$. From the definitions of these functions in eqs 2.20 and 2.21, we find

$$g(x) \approx 1 - \frac{1}{3}x \qquad \text{for } x \ll 1$$

$$r(x) \approx \frac{1}{6}x - \frac{1}{10}x^2 \qquad \text{for } x \ll 1$$

and

$$g(x) \approx 2/x \qquad \text{for } x \gg 1$$

$$r(x) \approx 4/x^2 \qquad \text{for } x \gg 1$$

Thus, the integral in eq 2.23 is dominated by the large k behavior. We therefore approximate the integrand by the large k asymptotics and upon straightforward integration obtain

$$\langle R^2\rangle = Nb^2\left(1 + \frac{2k_c v}{\pi^2 b^2}\right) \qquad (2.24)$$

Writing $k_c = 2\pi/\lambda$ and defining the packing length as $l = vb^{-2}$, we can rewrite the above result in the form

$$\langle R^2\rangle = Nb^2\left(1 + \frac{4l}{\pi\lambda}\right) \equiv Nb_{\mathrm{R}}^2 \qquad (2.25)$$

This result is essentially that given in eq 1.1.

The mean-square radius of gyration can be calculated following an approach similar to that above. Noting that

$$\langle R_g^2\rangle = \frac{1}{2N^2}\int_0^N ds \int_0^N dt\, \langle[\mathbf{R}(s) - \mathbf{R}(t)]^2\rangle \qquad (2.26)$$

we simply need to calculate $\langle[\mathbf{R}(s) - \mathbf{R}(t)]^2\rangle$ for arbitrary $0 < s, t < N$. This can be accomplished by introducing an auxiliary parameter $\eta_{s,t}$ which couples to $[\mathbf{R}(s) - \mathbf{R}(t)]^2$; the procedure is the same as the one used to calculate the mean-square end-to-end distance and will not be repeated here. However, we point out that while for an ideal Gaussian chain $\langle[\mathbf{R}(s) - \mathbf{R}(t)]^2\rangle \sim |s - t|$, the correction term due to the incompressibility constraint depends on s, t, and N in some rather complicated way (but approaches $|s - t|$ in the limit $N \rightarrow \infty$). Therefore, $\langle[R(s) - \mathbf{R}(t)]^2\rangle$ for the melt cannot be written in a way similar to eq 2.25. This fact suggests that the distribution of chain segment in a melt is not strictly Gaussian. Nevertheless, the overall mean-square radius of gyration, when evaluated using the asymptotic behavior of the integrand in the correction term, does scale with the mean-square end-to-end distance with the factor of $^1/_6$. Thus the effect of the incompressibility constraint for these aggregate properties is an upward renormalization of the Kuhn length from its value at the unperturbed state, the correction factor being given by eq 1.1.

The above calculation for the dimensions of a polymer chain in a single-component melt can be easily extended to the case of an athermal binary blend with volume fractions ϕ_1 and ϕ_2 for the two species ($\phi_1 + \phi_2 = 1$). In this case, to calculate the mean-square end-to-end distance of each polymer species, we introduce two auxiliary parameters η_1 and η_2 which couple to the square of the end-to-end distances of the two respective polymers. Following the same procedure that leads to eq 2.22, we arrive at the following free energy for an athermal binary blend

$$\Delta F(\eta_1,\eta_2) = \frac{V}{2(2\pi)^3}\int d\mathbf{k}\, \ln[\phi_1 N_1 v_1 g(x_1) + \phi_2 N_2 v_2 g(x_2)] + \frac{3}{2}n_1\eta_1 N_1 + \frac{3}{2}n_2\eta_2 N_2 + \frac{V}{2(2\pi)^3}\int d\mathbf{k}\, \frac{\eta_1\phi_1 N_1^2 v_1 r(x_1) + \eta_2\phi_2 N_2^2 v_2 r(x_2)}{\phi_1 N_1 v_1 g(x_1) + \phi_2 N_2 v_2 g(x_2)} \qquad (2.27)$$

where the notations should be self-explanatory. We note the first term on the right-hand side of eq 2.27 is simply the entropic correction to the Flory–Huggins free energy obtained by Fredrickson et al.[28] The mean-square end-to-end distance for polymer species i ($i = 1,2$) is obtained from eq 2.27 as

$$\langle R_i^2\rangle = \frac{2}{3}b_i^2 n_i^{-1}\left[\frac{\partial \Delta F(\eta_1,\eta_2)}{\partial \eta_i}\right]_{\eta_1=0,\eta_2=0} \tag{2.28}$$

Evaluating the integral in the correction term again using the large k asymptotic behavior of the integrand, we obtain

$$\langle R_i^2\rangle = N_i b_i^2\left(1 + \frac{4l_i}{\pi\lambda}\frac{l_i}{\bar{l}}\right) \equiv N_i b_{i\mathrm{R}}^2 \tag{2.29}$$

where $\bar{l} = \phi_1 l_1 + \phi_2 l_2$ is the volume fraction averaged packing length of the blend. The mean-square radius of gyration for each polymer can again be shown to be $^1/_6$ of the mean-square end-to-end distance, although the distribution at the segmental level is no longer strictly Gaussian.

3. Discussion

Equations 1.1 and 1.2 are the principal results of this paper. Our study shows that, contrary to Flory's prediction, the dimensions of a polymer in the melt are not the same as those of the unperturbed chain, the expansion factor being always larger than 1. The correction to the unperturbed chain dimension arises from the local packing constraint that exists in a dense liquid. In the framework of the present theory, the local packing constraint is modeled using a very simple incompressibility condition imposed on the melt, and the change of the chain dimension is reflected in the cut-off length scale associated with this incompressibility condition. Such a dependence on the cut-off length scale suggests that the local liquid structure may be important in determining the conformation and hence the dimension of a polymer in the melt state. A more accurate treatment of the liquid structure using, for example, the reference interaction site model[37–40] is necessary in order to fully incorporate these local effects.

A quantitative estimate of the correction to the unperturbed chain dimension requires knowledge of the cut-off length scale λ. In lattice models, it is natural to set λ to be the lattice spacing. Therefore, in principle, one can construct a lattice version of our calculation for predicting the dimension of a polymer on a lattice of self-avoiding and mutually avoiding polymers with no vacancies. Indeed, Monte Carlo simulations of dense polymer systems on a lattice[41] show that the dimension of a polymer is larger than that of both a random walk and a nonreversal random walk, consistent with our prediction.

For continuous systems, an accurate assessment of the cut-off length scale has to come from a theory which incorporates the local liquid structure. However, on physical grounds we expect that λ is on the order of the Kuhn length of the chain.[28] If we set $\lambda = b$ in eq 1.1, then we have $\langle R_g^2\rangle^{1/2}/\langle R_g^2\rangle_0^{1/2} = (1 + 4\pi^{-1}vb^{-3})^{1/2}$. For most polymers, v/b^3 is on the order 0.1. Thus the relative correction to the unperturbed dimension is on the order of 10%, which seems to be the range of discrepencies observed between the dimension of the chain in the melt and that at the Θ condition.[20] We should be cautious in relating the prediction of our study to the experimental observations, because of possible differences between a Θ chain and a truly ideal chain. On the other hand, the fact that both our theoretical prediction and the majority of the experimental data show positive deviations of the chain dimension from the reference states (unperturbed chain in our theory and Θ chain in experiments) suggests that the expansion effect predicted in this paper is probably a significant factor.

Even though the difference between the dimension of a polymer in a melt and that in the unperturbed state is not large, our theory indicates that local packing effects in the melt can be the source for the difference between the temperature coefficients at the two conditions and hence can contribute to the difference between the temperature coefficients in the melt and in Θ solvents. While a quantitative prediction is not possible at this point, owing to our lack of knowledge of the value and the temperature dependence of the cut-off length λ, our theory shows that the temperature dependence of the chain dimensions in the melt will involve the thermal expansion coefficient through the dependence of the chain dimensions on the specific volume of the polymer. The overall temperature coefficient is probably the result of a subtle balance between the bulk thermal expansion effect and the temperature dependence of the Kuhn length and the cut-off length.

Our eq 1.2 or eq 2.29 predicts that the chain dimension of a binary blend depends on the composition of the blend when the packing lengths of the two types of chains differ. A quantitative estimate again relies on our knowledge of the cut-off parameter λ which, in general, can be composition dependent. Some conclusions, however, can be drawn independently of the cut-off parameter. For example, it can be easily shown from eq 1.2 that

$$\frac{(b_{1\mathrm{R}}^2/b_1^2 - 1)}{(b_{2\mathrm{R}}^2/b_2^2 - 1)} = \frac{l_1^2}{l_2^2} \tag{3.1}$$

Thus, in an athermal binary blend, the polymer with the larger packing length will expand (relative to the unperturbed dimension) more than the polymer with the smaller packing length.

An interesting, related question concerns the change in the chain dimensions when two bulk polymer melts are mixed to form a blend. If we assume that λ is independent of the composition, then combining eqs 1.1 and 1.2, we find

$$\frac{b_{i\mathrm{R}}^2(\mathrm{blend})}{b_{i\mathrm{R}}^2(\mathrm{pure})} \approx 1 + \frac{4l_i}{\pi\lambda}\left(\frac{l_i}{\bar{l}} - 1\right) \tag{3.2}$$

Therefore, upon mixing, the polymer with the larger packing length will expand, whereas the polymer with the smaller packing length will contract. The possibility of changes in the β_i^2 parameter (the inverse of our packing length) in a blend from its pure component value has been suggested recently by Fredrickson.[42] Such changes are direct consequences of our findings here. Note that the change in the chain dimension of a polymer in a blend from its bulk value is rather small, which is perhaps the reason that such changes have been difficult to observe experimentally. However, at least one system, the polystyrene (PS)/poly(vinyl methyl ether) (PVME) blend,[29] seems to show the trend predicted by eq 3.2. The Kuhn lengths of the two polymers in their respective pure bulk states are almost identical,[43] but the monomeric volume (the volume of a Kuhn unit) of PS is larger than that of PVME.[44] Hence, PS has a larger packing length than PVME. Therefore, upon mixing, we expect the effective Kuhn length of PS to increase and that of the PVME to decrease. This is indeed the behavior inferred by Dudowicz and Freed[43] in their interpretation of the neutron scattering data of Han et al.[29] More recently, Briber et al.[45] have made direct neutron scattering measurements of the dimension of PS in PVME and found that the radius of gyration of PS is larger in PVME than in its own bulk, consistent with our prediction. Because the PS/PVME system is not an athermal mixture, this evidence should at best be regarded as a tentative support to the prediction of our theory.

We now discuss the disagreement between these findings and the result for the radius of gyration given by the structure factor of labeled chains calculated using the random phase approximation (RPA). The structure factor of labeled chains is in fact the measured quantity in SANS or other scattering experiments and is the basis for determining the radius of gyration using scattering techniques. We define the structure factor of the labeled chains as

$$S(k) = \frac{V^2}{n'Nv^2}\langle\hat{\phi}'(\mathbf{k})\,\hat{\phi}'(-\mathbf{k})\rangle \qquad (3.3)$$

where n' is the number of labeled chains, and $\hat{\phi}'(\mathbf{k})$ is the Fourier component of the corresponding volume fraction. (This definition ensures that, for noninteracting, ideal chains, $S(k)$ reduces to the single, ideal chain structure factor.) The radius of gyration of a labeled chain is then obtained, by taking the limit $n'/V \rightarrow 0$, from

$$\langle R_g^2\rangle = -\frac{3}{N}\left[\frac{\partial S(k)}{\partial k^2}\right]_{k=0} \qquad (3.4)$$

For an incompressible polymer melt, a calculation using RPA shows that, in the limit $n'/V \rightarrow 0$, $S(k)$ is the same as that of a noninteracting, ideal chain, namely,

$$S(k) = Ng(x) \qquad (3.5)$$

where $g(x)$ is the Debye function given by eq 2.20 with $x = Nb^2k^2/6$. Application of eq 3.4 then yields $\langle R_g^2\rangle = Nb^2/6$, the radius of gyration of the unperturbed chain.

The fact that the RPA structure factor yields the radius of gyration of the unperturbed chain should not come as a surprise, because in a sense RPA is a mean-field theory. However, we note that the RPA structure factor can also be derived using the same theoretical framework wherein we calculate the mean-square end-to-end distance. To compute the average in eq 3.3, we introduce a field J that couples to the microscopic volume fraction (or density) of the labeled chains and add the term $-V\sum_{k\neq 0}\hat{\phi}'(\mathbf{k})\,J(\mathbf{k})$ to the Hamiltonian $H_0(\mathbf{R})$ in eq 2.1. The correlation function $\langle\hat{\phi}'(\mathbf{k})\,\hat{\phi}'(-\mathbf{k})\rangle$ is then obtained from

$$\langle\hat{\phi}'_{\mathrm{A}}(\mathbf{k})\,\hat{\phi}'_{\mathrm{A}}(-\mathbf{k})\rangle = -V^{-2}\left[\frac{\partial^2 F(J)}{\partial J(\mathbf{k})\,\partial J(-\mathbf{k})}\right]_{J=0} \qquad (3.6)$$

where $F(J)$ is the free energy (scaled by $k_{\mathrm{B}}T$) of the melt with the generating field J. The calculation of $F(J)$ essentially follows the same steps that lead to $F(\eta)$. With the same Gaussian approximation as we made in calculating the mean-square end-to-end distance, and after some straightforward algebra, we arrive at the following expression for the free energy (of the single-component melt):

$$F(J) = F_0(0) + \frac{1}{2}\sum_{k\neq 0}\ln[Nvg(x)] - \frac{1}{2}V\sum_{k\neq 0}J(\mathbf{k})\,J(-\mathbf{k})\,\phi'(1-\phi')\,Nvg(x) \qquad (3.7)$$

where ϕ' is the volume fraction of the labeled chains. Using the definition of $S(k)$ and eq 3.6, we obtain the structure factor of the labeled chains as

$$S(k) = N(1-\phi')\,g(x) \qquad (3.8)$$

which in the limit $\phi' \rightarrow 0$ reduces to $S(k) = Ng(x)$.

We can in fact combine eqs 3.7 and 2.22 to write down a free energy which includes both the parameter η and the generating field J

$$F(\eta,J) = F_0(0) + \frac{1}{2}\sum_{\mathbf{k}\neq 0}\ln[Nvg(x)] + \frac{3}{2}n\eta N + \frac{1}{2}\eta N\sum_{\mathbf{k}\neq 0}\frac{r(x)}{g(x)} - \frac{1}{2}V\sum_{\mathbf{k}\neq 0}J(\mathbf{k})\,J(-\mathbf{k})\,\phi'(1-\phi')\,Nvg(x) + O(\eta^2,\eta J^2) \qquad (3.9)$$

The $O(\eta^2,\eta J^2)$ terms do not play any role for the calculation of the mean-square end-to-end distance or structure factor.

The paradox is then clear: the same free energy expression yields two different answers for the dimension of a chain in the melt state, when it is calculated using definitions that are different in form but identical in essence. If we accept the theoretical model for the melt, the only approximation we made in arriving at eq 3.9 is the Gaussian approximation invoked in the evaluation of the function G in eq 2.12. (In the presence of the generating field J, $\psi(-\mathbf{k})$ in eq 2.12 is replaced by $\psi(-\mathbf{k}) - iVJ(-\mathbf{k})$.) If higher order terms in ψ are included, the structure factor will be renormalized; this renormalization will bring the cut-off length into the structure factor and as a result the radius of gyration obtained from the renormalized structure factor will acquire a correction term that depends on the cut-off length. At the same time, these higher order terms will modify the $O(\eta)$ terms in the free energy, leading to an effective Kuhn length that can be different from the ones given by eq 1.1 (or eq 1.2 for the blend case). If we were able to keep the full ψ dependence in the function G, the two predictions on the chain dimension would be identical. In any case, however, we expect the $O(\eta)$ term in the free energy to be nonvanishing; thus there should be a correction to the chain dimension even if no approximations were made.

In light of the above discussion, especially of the expected renormalization due to higher order ψ terms, we propose a self-consistent Gaussian approximation, using the renormalized Kuhn length in the Gaussian approximation to the function G. This scheme will then give rise to a structure factor for the labeled chains that depends on the renormalized rather than the bare Kuhn length, and it is the renormalized rather than the bare radius of gyration that is measured from scattering experiments. The self-consistency condition requires

$$b_{\mathrm{R}}^2 = b^2(1 + 4l_{\mathrm{R}}/\pi\lambda) \qquad (3.10)$$

where the renormalized packing length $l_R = v/b_R^2$, with b_R being the renormalized Kuhn length. Thus eq 3.10 constitutes a self-consistent equation for b_R, which can be solved to yield

$$b_R^2 = \frac{b^2}{2}\left[1 + \left(1 + \frac{16v}{\pi\lambda b^2}\right)^{1/2}\right] \qquad (3.11)$$

Because the correction term is usually small, eq 3.11 can be approximated by eq 1.1. Similar self-consistent equations exist for the blend case.

Finally, we point out that our predictions (eqs 1.2 and 3.2) for the blends are non-RPA results. Therefore, the predicted effects could be missed by scattering experiments which use a finite fraction of labeled species based on the RPA recipe. A Zimm analysis, as used in the work of Briber et al.,[45] seems necessary.

In conclusion, we have shown that the dimensions of a polymer chain in the melt are larger than the corresponding unperturbed values. The correction arises from local packing constraints which are manifested by a cut-off length scale in a coarse-grained model. This length scale has hitherto been largely ignored or improperly treated in previous works which employ coarse-grained models. Our work shows that this local length scale can, in fact, affect large length scale properties such as the radius of gyration of a polymer and should be treated more carefully. Muthukumar[46] has recently suggested that the cut-off length scale may be important in determining the crossover between the weak and strong segregation limits of diblock copolymers.

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