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Polydispersity Variation and the Polymer Self-Diffusion Exponent

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ABSTRACT: We establish a general method of modeling polydispersity, its variation, and its effects. As a sample application of our idea, we reevaluate polydispersity effects as they occur in a novel test of reptation theory, the forced Rayleigh light scattering experiment of Leger et al.[2] In their study of the polymer self-diffusion coefficient, the analysis of polydispersity effects relies on the use of first cumulants to give an approximate treatment of molecular weight distribution averages and completely neglects the effects of polydispersity *variation*. In light of our model, we find that this can be considerably improved, even for the low polydispersities employed in their experiment. In order to redetermine the implications of their results, we find that it is essential not only to accurately calculate the molecular weight average of the monodisperse diffusion coefficient but also to properly compute the predicted decay in the density of the flash-excited pattern. As in our earlier paper concerning the molecular weight dependence of the zero-shear-rate viscosity, we again emphasize the general concept that the *rate of change* of polydispersity is more important than the polydispersity itself, as far the careful determination of exponents occurring in power-law molecular weight relations is concerned. Our model of the effects of polydispersity variation can be adapted and applied to any other experimental program where the type of molecular weight averaging which enters is known.

I. Introduction

The fundamental nature and appealing simplicity of the reptation model of de Gennes[1] make its applicability to entangled polymeric systems an important question. Leger et al.[2] have recently studied polystyrene chains in semidilute solution in order to test the prediction of reptation theory that the self-diffusion coefficient varies with molecular weight according to

$$D(M) \propto M^{-2} \tag{1.1}$$

Their experimental value for the self-diffusion coefficient exponent is quoted as 2 ± 0.1. This apparent confirmation of reptation theory contrasts with the problem of the zero-shear melt viscosity η, where several independent rheological studies[3-5] of the viscoelastic properties of polystyrene and other linear polymers seem to indicate an exponent of 3.4 in the power-law dependence of η on molecular weight. Reptation theory predicts an exponent of 3. In an earlier paper[6] we have found that this discrepancy cannot be explained away by polydispersity effects.

We have established a general approach to modeling the effects of polydispersity. The cornerstone of our method is to use a model molecular weight distribution to compute any required average over molecular weight. The first application of this simulation method was given in our preceding paper on the zero-shear viscosity. In the present paper we state our model and apply it to determine the nature and extent of these effects in self-diffusion coefficient studies.

When theory is compared with experiment, polydispersity effects always enter because actual measurements are performed on systems having a distribution of molecular weights. Although the very low polydispersities provided by fractionation and anionic polymerization can be taken advantage of to minimize the effects of molecular weight distribution, increasingly accurate experimental techniques justify and require the detailed examination of polydispersity effects even for systems of low polydispersity. The novel technique of forced Rayleigh light scattering employed by Leger et al. is a case in point, as we shall illustrate later in this paper.

There are two quite different aspects to the effects of polydispersity on the dynamics of concentrated polymeric systems. The first enters on the microscopic level and asks how the motions of a polymer chain are modified when the surrounding chains form a polydisperse medium rather than a monodisperse one. In the context of the original reptation model one could still claim that the chain only interacts with an averaged environment, specifically a confining tube. Therefore the molecular weight dependences derived for monodisperse systems would still be valid. Of course, this cannot be completely correct since the presence of very short chains probably reduces entanglement and reptation. At present there are no convincing extensions of the theory that address this question; the monodisperse relations are usually assumed.

The second aspect of polydispersity effects concerns the averaging over the molecular weight distribution when a macroscopic quantity is determined by the combined properties of the individual chains forming the distribution. The type of averaging that occurs seems obvious in some situations, but not at all in others. As an example of the latter, we consider the molecular weight dependence

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of the zero-shear viscosity in polymer melts as predicted by the model of Doi and Edwards.[7] As in the reptation model from which it is derived, the mean-field character of their model claims that the reptating chain interacts only with its average environment. The contributions made by individual chains to the constitutive equation are then additive, so that the effective tube renewal time for terminal-zone properties turns out to be the weight average[8] of the monodisperse tube renewal time $\tau(M) \propto M^3$. This leads to the prediction[9] $\eta \propto (M^*)^3$, where $M^* = (M_w M_z M_{z+1})^{1/3}$. However, we have reported in an earlier paper[6] that this prediction is completely inconsistent with experimental data[5] when critically tested at high polydispersities using polystyrene blends with bimodal molecular weight distributions. At present it is uncertain whether this amounts to a failure of the weight-averaging assumption, of the mean-field view that the predicted molecular weight dependence retains its monodisperse form even in a polydisperse medium, or of the underlying reptation model.[10]

Compared with rheological measurements, the type of macroscopic average occurring in the forced Rayleigh light scattering experiment of Leger et al. appears to be obvious. They follow the self-diffusion of polystyrene molecules by tagging them with photochromic monomers and use a pulse of interfering laser beams to generate a spatially periodic pattern consisting of excited tags. The scattering amplitude of the resulting absorption grating is proportional to the number of excited chromophores multiplied by a decay function representing the smearing of the grating due to spatial diffusion of the labeled chains. In a polydisperse medium the net scattering amplitude is provided by the number average of the monodisperse decay function, there being two photochromic molecules on each tagged polystyrene chain regardless of molecular weight (see eq 3.1–3.3).

In this paper we use this averaging assumption to study polydispersity effects in the experiment of Leger et al. These workers also considered polydispersity effects, although less extensively and with the aid of approximations. Because our model of polydispersity effects uses well-defined molecular weight distributions, it enables us to avoid such approximations and to accurately evaluate the extent of these effects. We outline our model and its main implications in section II and apply it to the Leger experiment in section III. Although the quantitative conclusions of our paper are restricted to the experiment of Leger et al., we emphasize that our approach is generally applicable to any experiment where one knows the type of molecular weight averaging. Since our analysis reveals that these effects are non-trivial in form even for the low polydispersities encountered by Leger et al., our method should be kept in mind as the proper way of thinking about polydispersity effects in other situations.

II. Method of Modeling Polydispersity and Gauging Its Effects

We examine polydispersity effects by using model molecular weight distributions. This enables us to explicitly compute any molecular weight average without the need for approximations. A model distribution is itself idealized, but it serves as an excellent means of revealing the true nature of any polydispersity effects and of estimating their probable extent. The model distributions which we employ in actual calculations are the log-normal and Schulz models.[11] These give a reasonable description of the molecular weight distribution in anionically polymerized polystyrenes (which are used in many studies), as illustrated in our earlier paper.[6]

The central concept developed in our previous paper is that the *rate of variation* of polydispersity is more important than the polydispersity itself, as far as the adjustment of exponents occurring in power laws is concerned.

To resubstantiate this, we make the key assumption that the molecular weight distributions have a *form* which is fixed throughout the set of samples. This is a reasonable simplification since most experimental studies deal with samples that have each been obtained by the same procedures. By this assumption we actually mean that the molecular weight distributions form a two-parameter family, with one parameter, such as the weight-average molecular weight M_w, setting the molecular weight scale, and the other parameter determining the width of the distribution. For the latter parameter we use the standard polydispersity measure

$$P = M_w/M_n \tag{2.1}$$

The parametric form of our model molecular weight distributions is indicated by

$$n(M) = n_{M_w,P}(M) \tag{2.2}$$

where we have employed the number distribution for concreteness.

Next, we consider the behavior of a molecular weight average of a given physical quantity Q, which is related to molecular weight in a monodisperse system by a general power law

$$Q(M) \propto M^{-\alpha} \tag{2.3}$$

with an intrinsic exponent α. We now suppose that the type of molecular weight average which is observed is the number average of Q

$$\langle Q(M) \rangle \propto \int M^{-\alpha} n_{M_w,P}(M) \, \mathrm{d}M \tag{2.4}$$

If we scale by the weight-average molecular weight and define the dimensionless molecular weight

$$m \equiv M/M_w \tag{2.5}$$

then eq 2.4 becomes

$$\langle Q(M) \rangle \propto M_w^{-\alpha} g(P,\alpha) \tag{2.6}$$

where

$$g(P,\alpha) \equiv \int m^{-\alpha} \tilde{n}_P(m) \, \mathrm{d}m \tag{2.7}$$

and

$$\tilde{n}_P(m) \equiv n_{M_w,P}(M) M_w \tag{2.8}$$

It is important to note that, since the weight-average molecular weight is incorporated in the dimensionless molecular weight m, the dimensionless number distribution $\tilde{n}_P(m)$ is parametrized only by the polydispersity. Thus the effects of polydispersity are completely contained in the function $g(P,\alpha)$, called the polydispersity correction. This shows that for *constant* polydispersity, the number-averaged quantity $\langle Q(M) \rangle$ is characterized by the *same* intrinsic exponent α assumed for monodisperse conditions. This result would also hold if the number average $\langle Q(M) \rangle$ were expressed in terms of a molecular weight average other than M_w or even if the type of molecular weight average defining $\langle Q(M) \rangle$ were different, since only $g(P,\alpha)$ would change.

However, if the polydispersity *varies* with molecular weight, then the exponent is *modified*. Except under special circumstances, it is also no longer a constant and $\langle Q(M) \rangle$ does not obey a true power law. When the polydispersity P varies, let us assume it to be a well-defined

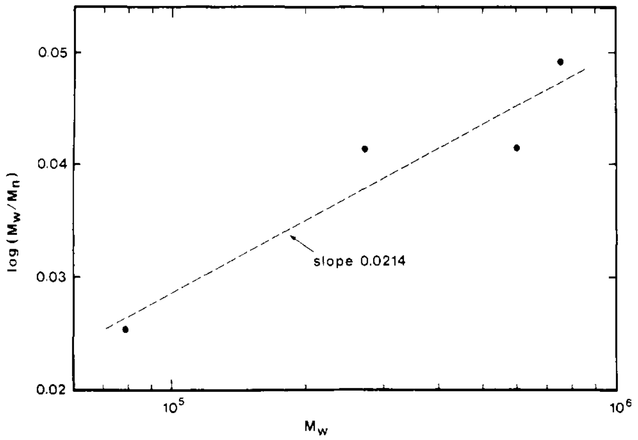

Figure 1. Dependence of the polydispersity $P = M_w/M_n$ on weight-average molecular weight M_w for the polydisperse samples studied by Leger et al.[2] Dashed line: least-squares fit $P \propto M_w^{0.0214}$, defining the systematic component of the polydispersity variation.

function $P(M_w)$ of molecular weight throughout the set of samples. This assumption merely enables us to isolate the systematic effects of variable polydispersity. It allows us to continue to regard $\langle Q(M) \rangle$ as a definite function of M_w and to define the local exponent

$$\alpha(M_w) \equiv -\frac{\partial \ln \langle Q(M) \rangle}{\partial \ln M_w} = \alpha - \frac{\partial \ln P}{\partial \ln M_w} \frac{\partial \ln g(P,\alpha)}{\partial \ln P} \qquad (2.9)$$

This equation shows that the *rate of polydispersity variation*, *c*, where

$$c \equiv \partial \ln P / \partial \ln M_w \qquad (2.10)$$

rather than the polydispersity, is the essential factor determining the modified power-law exponent of a quantity which is subject to molecular weight averaging. Of course, the polydispersity itself does enter eq 2.9 through the polydispersity correction $g(P,\alpha)$, and significant departures from a power law will usually occur when P is large, but a nonzero variation in the polydispersity is a necessary condition for any shift in the exponent.

The assumption of a smooth variation of molecular weight distribution from sample to sample embodied in eq 2.9 and 2.10 has been made only for the sake of exhibiting the systematic effects of polydispersity variation. In actual practice the polydispersity does not vary smoothly from sample to sample, but nevertheless there is often a correlation between molecular weight and polydispersity (see Figure 1). The effects of this correlation are in fact contained in the above analysis. This is illustrated in our previous paper on the zero-shear viscosity, where we compute shifts of the viscosity exponent in two different ways. The first corresponds to the above approach and assumes a smooth variation in polydispersity, given by the mean slope of the log P – log M_w curve for the set of samples. In the second, the actual viscosity–molecular weight data were adjusted at each data point according to the individual polydispersities, and a new least-squares fit was made. The two approaches gave essentially identical results for the viscosity exponent shift, demonstrating the practical utility of eq 2.9 and 2.10. Otherwise, in situations where the polydispersity varies randomly with molecular weight, there is a corresponding lack of correlation of $\langle Q(M) \rangle$ with average molecular weight, and the consideration of polydispersity effects is irrelevant from the very outset.

The above viewpoint and model are illustrated below, where we consider the effect of polydispersity on the forced Rayleigh light scattering measurements of Leger et al.[2] In this case, $Q(M)$ becomes the intrinsic self-diffusion coefficient $D(M)$. Because only the modified exponent $\alpha(M_w)$ is experimentally accessible when studying polydisperse systems, it is necesary to apply eq 2.9 and include the rate of polydispersity variation, c, to determine the intrinsic or monodisperse exponent α.

III. An Example: Analysis of the Forced Rayleigh Light Scattering Experiment

The forced Rayleigh light scattering experiment of Leger et al.[2] uses semidilute solutions of polystyrene samples in which a fraction of the polymers are tagged with photochromic monomers. Flash excitation by interfering laser beams produces a spatially periodic pattern of photoexcited tags, which subsequently smears due to spatial diffusion of the labeled chains. The decay is studied by using the excitation pattern as an absorption grating for a coherent readout beam. Measurement of the strength of the diffracted light signal as a function of time then determines an average diffusion coefficient $\langle D(M) \rangle$.

We now discuss the type of average defining $\langle D(M) \rangle$. In the model employed by Leger et al., the scattering amplitude of the flash-excited grating for a monodisperse system relaxes in proportion to

$$A_{\mathbf{q},M}(t) = \exp[-\Gamma_{\mathbf{q}}(M)t] \qquad (3.1)$$

with a rate of decay

$$\Gamma_{\mathbf{q}}(M) = D(M)\mathbf{q}^2 + \Gamma_{\text{deex}} \qquad (3.2)$$

In this equation, $\mathbf{q}$ is the adjustable wavevector of the grating and $D(M)$ is the self-diffusion coefficient at molecular weight M. The pattern also decays in situ by spontaneous deexcitation of the photochromic monomers, giving the additional contribution Γ_{deex} to the overall decay rate. Since the system is polydisperse, the actual erasure of the grating is given by averaging the grating amplitude $A_{\mathbf{q},M}(t)$ over the molecular weight distribution. As discussed in the Introduction, the true relaxation is described by

$$\langle A_{\mathbf{q},M}(t) \rangle \equiv \int A_{\mathbf{q},M}(t) n(M) \, \mathrm{d}M \qquad (3.3)$$

The average is taken over the *number* distribution $n(M)$ because the number of photochromic molecules per labeled chain is independent of chain length.

Leger et al. assume that the number-averaged grating amplitude $\langle A_{\mathbf{q},M}(t) \rangle$ is well-represented by a single exponential; i.e.

$$\langle A_{\mathbf{q},M}(t) \rangle \simeq \exp[-\langle \Gamma_{\mathbf{q}}(M) \rangle t] \qquad (3.4)$$

This result is obtained immediately from eq 3.1 when the cumulant expansion method[12] is applied to lowest order. By eq 3.2, the resulting average decay rate $\langle \Gamma_{\mathbf{q}}(M) \rangle$ is predicted to have the form

$$\langle \Gamma_{\mathbf{q}}(M) \rangle = \langle D(M) \rangle \mathbf{q}^2 + \Gamma_{\text{deex}} \qquad (3.5)$$

Since the type of average occurring in this equation is the same as in eq 3.3, the average diffusion coefficent $\langle D(M) \rangle$ in the single-exponential approximation is the number average of the monodisperse diffusion coefficient:

$$\langle D(M) \rangle \equiv \int D(M) n(M) \, \mathrm{d}M \qquad (3.6)$$

A. Number-Averaged Self-Diffusion Coefficient. The single-exponential approximation for the number-averaged grating amplitude is crucial to the result in eq 3.6. In section IIIB we will consider its accuracy by using our model molecular weight distributions to compute the actual decay contained in eq 3.3. But for the moment we

Table I
Expressions for the Dimensionless Number Distribution $\tilde{n}_P(m)$ and the Polydispersity Correction $g(P,\alpha)$ for the Log-normal and Schulz Model Molecular Weight Distributions[a]

model MWD	$\tilde{n}_P(m)$	$g(P,\alpha)$
log-normal	$\dfrac{1}{P(2\pi \ln P)^{1/2}} m^{-2} \times$ $\exp[-\ln^2 (mP^{1/2})/2 \ln P]$	$P^{(\alpha^2+3\alpha)/2}$
Schulz	$\dfrac{(b+2)^{b+1}}{\Gamma(b+1)} m^b \times$ $\exp[-(b+2)m]$	$[P/(P-1)]^{\alpha} \times$ $\dfrac{\Gamma[1/(P-1)-\alpha]}{\Gamma[1/(P-1)]}$

[a] For the Schulz model, the polydispersity P is related to the parameter b by $P = (b+2)/(b+1)$, and Γ is the gamma function.

retain this approximation and derive a preliminary value for the intrinsic self-diffusion coefficient exponent. We accomplish this by comparing the observed molecular weight dependence of the average diffusion coefficient, which was quoted in terms of the particular average molecular weight $[M_wM_n]^{1/2}$ by Leger et al. as

$$\langle D(M)\rangle_{\text{obsd}} \propto ([M_wM_n]^{1/2})^{-2.05\pm0.1} \tag{3.7}$$

with the molecular weight dependence predicted from our model of polydispersity effects.

We assume that, in its monodisperse form, the self-diffusion coefficient obeys the general power law

$$D(M) = KM^{-\alpha} \tag{3.8}$$

with the intrinsic self-diffusion coefficient exponent α to be determined. For a general two-parameter model molecular weight distribution, eq 2.6 shows that the number-averaged diffusion coefficient has the predicted molecular weight dependence

$$\langle D(M)\rangle = KM_w^{-\alpha}g(P,\alpha) \tag{3.9}$$

The specific from of the polydispersity correction $g(P,\alpha)$ depends on the choice of model molecular weight distribution and is determined by eq 2.7. Table I shows the form of the dimensionless number distribution $\tilde{n}_P(m)$ and the resulting polydispersity correction for the two distributions employed in our study, the log-normal and the Schulz models. For the log-normal model we then find

$$\langle D(M)\rangle \propto M_w^{-\alpha}P^{(\alpha^2+3\alpha)/2} \tag{3.10}$$

This can be reduced to a dependence on M_w alone, if we characterize the polydispersity variation by a well-defined function $P(M_w)$. As discussed in section II, this procedure focuses on the systematic effects of polydispersity variation, and it is these effects that are responsible for shifting the self-diffusion coefficient exponent. For the samples studied by Leger et al. we have made a log–log plot of P against M_w in Figure 1 and find a correlation between polydispersity and molecular weight which has a power-law dependence

$$P \propto M_w^{c} \tag{3.11}$$

with a constant rate of polydispersity variation (see eq 2.10)

$$c = 0.0214 \tag{3.12}$$

This value is obtained from a uniformly weighted least-squares fit. Thus when the samples studied by Leger et al. are modeled by the log-normal distribution, the average diffusion coefficient is predicted to have a power-law dependence on M_w

$$\langle D(M)\rangle \propto M_w^{-\alpha(M_w)} \tag{3.13}$$

with a fixed exponent

$$\alpha(M_w) = \alpha - c(\alpha^2 + 3\alpha)/2 \tag{3.14}$$

which is independent of polydispersity.

To determine the value of the intrinsic self-diffusion coefficient exponent α implied by the data of Leger et al., we first reexpress the predicted molecular weight dependence contained in eq 3.13 and 3.14 in terms of the average molecular weight $[M_wM_n]^{1/2}$ From eq 2.1 and 3.11 we have

$$M_w \propto ([M_wM_n]^{1/2})^{2/(2-c)} \tag{3.15}$$

Therefore the predicted $\langle D(M)\rangle$ can also be written

$$\langle D(M)\rangle \propto ([M_wM_n]^{1/2})^{-\alpha([M_wM_n]^{1/2})} \tag{3.16}$$

where

$$\alpha([M_wM_n]^{1/2}) = 2[\alpha - c(\alpha^2 + 3\alpha)/2]/(2-c) \tag{3.17}$$

Note that when the intrinsic exponent α is given the value 2 predicted by the reptation model, we get $\alpha([M_wM_n]^{1/2}) = 2 - 4c + O(c^2)$, compared with the previous result $\alpha([M_wM_n]^{1/2}) = 2$ obtained by Leger et al. neglecting polydispersity variation. This is an explicit example of the importance of the *rate of polydispersity variation*, rather than the polydispersity, in determining corrections to power-law exponents.

As our final step we identify the predicted average diffusion coefficient $\langle D(M)\rangle$ with the observed value $\langle D(M)\rangle_{\text{obsd}}$ and equate the corresponding exponents in eq 3.7 and 3.17. The resulting equation for α is

$$\alpha = 2.05 + c[(\alpha^2 + 3\alpha)/2 - 2.05/2] \tag{3.18}$$

This has the approximate solution

$$\alpha \simeq 2.05 + 4c \tag{3.19}$$

which shows that α exceeds 2.05 when the polydispersity increases with molecular weight. Using the rate of polydispersity variation given in eq 3.12 and solving eq 3.18 exactly, we find that in the present discussion the intrinsic self-diffusion coefficient exponent in the log-normal model is given by

$$\alpha = 2.15 \tag{3.20}$$

It is a special property of the log-normal distribution that the modified exponents $\alpha(M_w)$ and $\alpha([M_wM_n]^{1/2})$ for the average diffusion coefficient are constant and independent of polydispersity. In contrast, the Schulz model gives a polydispersity correction $g(P,\alpha)$, which is not a simple power of the polydispersity. Consequently, the predicted average diffusion coefficient no longer has a simple power-law dependence on M_w, and it is necessary to work with the varying exponent defined by eq 2.9. In terms of the weight-average molecular weight M_w we have

$$\alpha(M_w) \equiv -\frac{\partial \ln \langle D(M)\rangle}{\partial \ln M_w} = \alpha - c\frac{\partial \ln g(P,\alpha)}{\partial \ln P} \tag{3.21}$$

Referring to Table I, we find that the logarithmic derivative of $g(P,\alpha)$ is

$$\frac{\partial \ln g(P,\alpha)}{\partial \ln P} = -\frac{1}{P-1}\left\{\alpha + \frac{P}{P-1}(\psi[1/(P-1) - \alpha] - \psi[1/(P-1)])\right\} \tag{3.22}$$

where ψ is the digamma function. To check the amount of variability in $\alpha(M_w)$ across the range of P values encountered by Leger et al., we follow the equivalent procedure of fixing $\alpha(M_w)$ and solving eq 3.21 for α at each value of P. The observed value of $\alpha(M_w)$ is obtained by combining eq 3.7 and 3.15. It is

$$\alpha(M_w)_{\rm obsd} \equiv -\partial \ln \langle D(M) \rangle_{\rm obsd}/\partial \ln M_w = 2.05(1 - c/2) \qquad (3.23)$$

Equating eq 3.23 and 3.21, we then find $\alpha = 2.16$ and 2.18 for $P = 1.06$ and 1.12, respectively. Thus for the Schulz model we conclude that the intrinsic self-diffusion coefficient exponent has a value close to

$$\alpha = 2.17 \qquad (3.24)$$

Although not identical with the correction computed from the log-normal model in eq 3.20, the correction provided by the Schulz model is very similar.

We emphasize that the above results for the intrinsic self-diffusion coefficient exponent α are applicable only when the type of average diffusion coefficient being measured is the number average, eq 3.6. This depends on the accuracy of the single-exponential approximation, eq 3.4, for the number-averaged grating amplitude $\langle A_{\mathbf{q},M}(t) \rangle$. We now consider this question.

B. Number-Averaged Grating Amplitude. In a polydisperse system, the net scattering amplitude for the flash-excited grating in the forced Rayleigh light scattering experiment is the number average $\langle A_{\mathbf{q},M}(t) \rangle$ of the monodisperse grating amplitude $A_{\mathbf{q},M}(t)$ (see eq 3.3). One way to compare $\langle A_{\mathbf{q},M}(t) \rangle$ with the approximation of a single exponential, eq 3.4, is to define an effective decay rate $\Gamma_{\rm eff}(t) = -\partial \ln \langle A_{\mathbf{q},M}(t) \rangle/\partial t$, which is the tangent slope of the decay curve on a semilog plot. In the single-exponential approximation for the decay, $\Gamma_{\rm eff}(t)$ reduces to the number-averaged decay rate $\langle \Gamma_{\mathbf{q}}(M) \rangle$. However, with the proper decay curve we use eq 3.3 and find

$$\Gamma_{\rm eff}(t) = \langle \Gamma_{\mathbf{q}}(M) \exp[-\Gamma_{\mathbf{q}}(M)t] \rangle / \langle \exp[-\Gamma_{\mathbf{q}}(M)t] \rangle \qquad (3.25)$$

where $\langle \cdots \rangle$ denotes the number average. Thus the effective decay rate is time-dependent, and only at $t = 0$ does the number-averaged decay rate $\langle \Gamma_{\mathbf{q}}(M) \rangle$ accurately characterize the actual decay curve.

To more fully compare the shape of the number-averaged decay with that of the single-exponential approximation, we compute $\langle A_{\mathbf{q},M}(t) \rangle$ using the log-normal model molecular weight distribution and plot $\ln \langle A_{\mathbf{q},M}(t) \rangle$ vs. time in Figure 2 for the upper polydispersity value $P = 1.12$ encountered by Leger et al. The dashed line is the decay curve predicted by the single-exponential approximation. It is evident that a serious deviation from exponential decay is present even for this low polydispersity. The nonexponential tail represents a decrease in the effective decay rate, produced by the slower diffusion rates of the longer chains in the molecular weight distribution. Note that in constructing Figure 2, we ignored the contribution made by $\Gamma_{\rm deex}$ to $\Gamma_{\mathbf{q}}(M)$ because the determination of the average diffusion coefficient by Leger et al. was effectively based on the rate of decay at large $|\mathbf{q}|$, where diffusional smearing dominates spontaneous deexcitation of the chromophores. We also used the dimensionless time and decay rate variables

$$\tilde{t} = K\mathbf{q}^2 M_w^{-\alpha} t \qquad (3.26)$$

and

$$\tilde{\Gamma}(m) = [K\mathbf{q}^2 M_w^{-\alpha}]^{-1} \Gamma_{\mathbf{q}}(M) = m^{-\alpha} \qquad (3.27)$$

(see eq 2.5, 3.2, and 3.8). This removes the $\mathbf{q}$ and M_w dependence common to all samples and allows us to focus on the effects of polydispersity. It also enables us to rewrite eq 3.3 for $\langle A_{\mathbf{q},M}(t) \rangle$ as

$$\langle A_{\mathbf{q},M}(t) \rangle = \int_0^\infty \exp(-m^{-\alpha}\tilde{t}) \tilde{n}_P(m) \, dm \qquad (3.28)$$

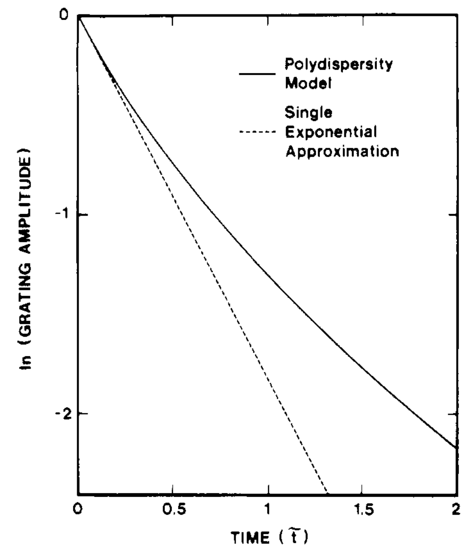

Figure 2. Plot of the natural log of the number-averaged grating amplitude $\langle A_{\mathbf{q},M}(t) \rangle$ (see eq 3.3) against time in dimensionless units, showing the deviation from single-exponential decay for a polydispersity $M_w/M_n = 1.12$. Computed using the log-normal model molecular weight distribution.

where $\tilde{n}_P(m)$ is the dimensionless number distribution introduced in section II. To obtain the curve in Figure 2 we computed this integral numerically. A faster method, which proves to be sufficiently accurate for low polydispersities, is the Gaussian approximation to the integral (see Appendix A).

A quantitative measure of the deviation of $\langle A_{\mathbf{q},M}(t) \rangle$ from single-exponential decay is the rate of decrease of $\tilde{\Gamma}_{\rm eff}(\tilde{t})$ at $\tilde{t} = 0$. Using eq 3.25–3.28, one can readily express this as

$$-\partial \ln \tilde{\Gamma}_{\rm eff}(\tilde{t})/\partial \tilde{t}|_{\tilde{t}=0} = g(P,2\alpha)/g(P,\alpha) - g(P,\alpha) \qquad (3.29)$$

where $g(P,\alpha)$ is the polydispersity correction, defined in eq 2.7 and given in Table I. For the log-normal model with $\alpha = 2$, we find

$$-\partial \ln \tilde{\Gamma}_{\rm eff}(\tilde{t})/\partial \tilde{t}|_{\tilde{t}=0} = P^5(P^4 - 1) \qquad (3.30)$$

which has the values 0.351 and 1.01 for $P = 1.06$ and $P = 1.12$, respectively. This shows explicitly why the deviation of the computed decay from single-exponential decay illustrated in Figure 2 is so severe, even for low polydispersities. Clearly, there is serious doubt about the validity of any analysis of the observed decay curves which is based on the assumption of single-exponential decay.

C. Reinterpreting the Average Diffusion Coefficient. The introductory discussion in this section makes it clear that if the number-averaged grating amplitude $\langle A_{\mathbf{q},M}(t) \rangle$ is well-approximated by a single decaying exponential (see eq 3.4), the forced Rayleigh light scattering experiment of Leger et al. yields an average decay rate having the form of eq 3.5, from which a specific type of average diffusion coefficient can be extracted. This is the number-averaged diffusion coefficient, eq 3.6. Relying on this approximation in section IIIA, we examined the effect of polydispersity on the intrinsic self-diffusion coefficient exponent α (see eq 3.8) by using model molecular weight distributions to compute the number average of $D(M)$ exactly. This gave an apparent value for α of about 2.15 in the experiment of Leger et al.

However, this result is only preliminary since our model of the molecular weight distribution enables us to extend our analysis by computing the form of the number-averaged grating amplitude $\langle A_{\mathbf{q},M}(t) \rangle$, using eq 3.1–3.3. The results in section IIIB demonstrate that the computed decay curves are *not* well-approximated by single-exponential decay. Furthermore, the computed decay curves only yield a number-averaged decay rate when one extracts the initial slope of the decay curve (see eq 3.25). Therefore, since the data analysis performed by Leger et al. is instead based on an exponential fit to the complete decay curve, the type of average self-diffusion coefficient that is measured is not the number average. Additional analysis is required to determine the value of the intrinsic self-diffusion coefficient exponent implied by their experiment.

While one should fit the experimental data of Leger et al. using our computed, nonexponential form of $\langle A_{\mathbf{q},M}(t)\rangle$ (assuming a log-normal distribution) and thereby determine the intrinsic self-diffusion coefficient exponent directly, we find an indirect method more conventient in the absence of the actual data. Our approach is to give a proper interpretation of the results of their fitting procedure. To do this we simulate the observed decay using our computed $\langle A_{\mathbf{q},M}(t)\rangle$ and then apply their single-exponential fitting method. This procedure gives the expected molecular weight dependence of their observed average diffusion coefficient based on our model. By equating this with the observed molecular weight dependence in eq 3.7, we extract a value for α.

To use the computed number-averaged grating amplitude $\langle A_{\mathbf{q},M}(t)\rangle$ in simulating the observed decay, we first recall that the Leger experiment measures the decay of the *intensity*, $S(t)$, of light diffracted from the excitation pattern. We then model the observed intensity by

$$S_{\mathrm{mod}}(t) = [a'\langle A_{\mathbf{q},M}(t)\rangle + b']^2 + c' \qquad (3.31)$$

where a' is a proportionality factor that converts grating amplitude to diffracted light amplitude, b' is the amplitude of the coherent background, and c' is the intensity of the incoherent background. Due to signal averaging, the background levels in the Leger experiment are low, and we found that the corresponding values of b'/a' and c'/a' could be reset to zero without much effect on the final inferred value for the intrinsic self-diffusion coefficient exponent. Therefore we simplify the remaining discussion by putting $b' = c' = 0$. There is no loss of generality in setting $a' = 1$, so we have

$$S_{\mathrm{mod}}(t) = \langle A_{\mathbf{q},M}(t)\rangle^2 \qquad (3.32)$$

As do Leger et al. in fitting the observed intensity $S(t)$, we fit the *model* intensity in eq 3.32 by using a single exponential in place of $\langle A_{\mathbf{q},M}(t)\rangle$ in eq 3.31 to give

$$S_{\mathrm{fit}}(t) = [a \exp(-\Gamma_{\mathrm{fit}}t) + b]^2 + c \qquad (3.33)$$

To reduce the number of parameters, we set either b or c to zero and impose the condition $S_{\mathrm{fit}}(t = 0) = S_{\mathrm{mod}}(t = 0)$. This implies $b = 1 - a$ or $c = 1 - a^2$ for $c = 0$ or $b = 0$, respectively. At least one of the background level parameters must be nonzero in order to account for the nonexponential tail in $S_{\mathrm{mod}}(t)$. Over a noninfinite time interval this tail results in an apparent background level.

Our least-squares fitting procedure minimizes the quantity

$$\chi^2 = \int_0^{t_{\max}} \{S_{\mathrm{mod}}(t) - S_{\mathrm{fit}}(t)\}^2/\sigma^2(t)\,\mathrm{d}t \qquad (3.34)$$

with respect to the parameters a and Γ_{fit}. Since the actual intensity was measured by counting methods, we must give less weight to the tail of the decay curves where the counting rate was low. Consequently, we substitute $\sigma^2(t) = S_{\mathrm{mod}}(t)$. The upper limit $t_{\max}$ on the integration is the duration of the measurement. From Figure 2 we see that in dimensionless units $\tilde{t}_{\max} = 2$ covers just over 2 time constants of decay (in terms of amplitude), corresponding to the intervals employed in the Leger experiment.[2]

Because our method of fit corresponds to that employed by Leger et al. in fitting their original data, we assert that our fitted decay rates Γ_{fit} must correspond to their observed decay rates Γ_{obsd}. From eq 3.5, the observed decay rate at large grating wavevector has the form $\Gamma_{\mathrm{obsd}} = \langle D(M)\rangle_{\mathrm{obsd}}\mathbf{q}^2$. Using eq 3.27, we find that Γ_{fit} has the form $\Gamma_{\mathrm{fit}} = K\mathbf{q}^2M_{\mathrm{w}}^{-\alpha}\tilde{\Gamma}_{\mathrm{fit}}(P,\alpha)$, where $\tilde{\Gamma}_{\mathrm{fit}}(P,\alpha)$ denotes the dimensionless fitted decay rate at the given values of P and α. If we write $\Gamma_{\mathrm{fit}} = \langle D(M)\rangle\mathbf{q}^2$, then we can identify the proper form of the predicted average diffusion coefficient. It is

$$\langle D(M)\rangle = KM_{\mathrm{w}}^{-\alpha}\tilde{\Gamma}_{\mathrm{fit}}(P,\alpha) \qquad (3.35)$$

Evidently $\tilde{\Gamma}_{\mathrm{fit}}(P,\alpha)$ is the analogue of the earlier polydispersity correction $g(P,\alpha)$ in eq 3.9, where $\langle D(M)\rangle$ was taken to be the number average of $D(M)$.

To determine the value of the intrinsic self-diffusion coefficient exponent α, we compare the predicted and observed molecular weight dependence by differentiating the equation $\langle D(M)\rangle = \langle D(M)\rangle_{\mathrm{obsd}}$ with respect to M_{w}. As expected from the complexity of the averaging, the predicted molecular weight dependence in $\langle D(M)\rangle$ is not that of a simple power law, and we must work with the local self-diffusion coefficient exponent $\alpha(M_{\mathrm{w}}) = -\partial \ln \langle D(M)\rangle / \partial \ln M_{\mathrm{w}}$. Following the same procedure as at the end of section IIIA, we obtain

$$\alpha(M_{\mathrm{w}}) = \alpha - c(\partial \ln \tilde{\Gamma}_{\mathrm{fit}}(P,\alpha)/\partial \ln P) = 2.05(1 - c/2) = \alpha(M_{\mathrm{w}})_{\mathrm{obsd}} \qquad (3.36)$$

The solution of this equation gives the value of the intrinsic self-diffusion coefficient exponent α which is implied by the results of Leger et al., accounting for the computed form of the number-averaged grating amplitude and avoiding the single-exponential approximation.

We solve eq 3.36 numerically by using a minimization program to compute $\tilde{\Gamma}_{\mathrm{fit}}(P,\alpha)$ as a function of P and α. We then obtain the following result for both the log-normal and Schulz model molecular weight distributions:

$$P = 1.06 \Rightarrow \alpha = 2.13$$
$$P = 1.12 \Rightarrow \alpha = 2.11 \qquad (3.37)$$

These values were obtained when the duration of the measurement was assumed to be $\tilde{t}_{\max} = 2$ and slowly increase when $\tilde{t}_{\max}$ is decreased. It is necessary to consider different polydispersity values in order to discover the amount of departure from an exact power law. The variability in the intrinsic exponent α arises because eq 3.36 is solved under the condition of a constant observed exponent $\alpha(M_{\mathrm{w}})_{\mathrm{obsd}}$, the value of which is given in eq 3.23. If α was fixed instead, very nearly the same variation would be seen in the predicted value of $\alpha(M_{\mathrm{w}})$. Since the variation of α with P and $\tilde{t}_{\max}$ is small in comparison with the experimental uncertainty of ±0.1 in $\alpha(M_{\mathrm{w}})_{\mathrm{obsd}}$, we quote a single final value for the intrinsic self-diffusion coeffcient exponent. It is

$$\alpha = 2.1 \pm 0.1 \qquad (3.38)$$

The uncertainty in α is directly transferred from $\alpha(M_{\mathrm{w}})_{\mathrm{obsd}}$ because α varies almost linearly with $\alpha(M_{\mathrm{w}})_{\mathrm{obsd}}$ when eq 3.36 is solved.

The fitted intensity curves $S_{\mathrm{fit}}(t)$ that minimize χ^2 and yield $\tilde{\Gamma}_{\mathrm{fit}}(P,\alpha)$ are found to give a very good fit to the computed model intensity curves $S_{\mathrm{mod}}(t)$. The fit which assumes $c = 0$ (and $b = 1 - a$) gives lower minimum χ^2 values than the choice $b = 0$. Using a discrete sum over $N = 200$ uniformly spaced t values in the interval $(0,t_{\max})$, we find a small error per data point of $(\chi^2/N)^{1/2} = 10^{-2}$ and $(\chi^2/N)^{1/2} = 2 \times 10^{-2}$ for $P = 1.06$ and $P = 1.12$, respectively. These errors are comparable with those found by Leger et al. in fitting their original data, indicating that our analysis gives a good simulation of their fitting procedure. It is important to note as well that the closeness of the fit is not a justification of the single-exponential approximation. Rather, the nonexponential character of the observed decay is fitted well only because the single exponential is supplemented by nonzero background levels. These levels are required even in the absence of true background levels (see eq 3.32) and are found to be $b = 0.07$ and $b = 0.11$ for $P = 1.06$ and $P = 1.12$, respectively. The increase in χ^2 with P indicates that a single exponential would be unsuitable for fitting the observed decay curves at higher polydispersities. In this case it would be necessary to fit the experimental data directly with our computed number-averaged grating amplitude and eq 3.31.

IV. Conclusion

In this paper we have stated our method of modeling polydispersity and of evaluating its effects on the measurement of molecular weight dependences. Quite generally, we find that the *rate of variation* of polydispersity is the key factor governing the adjustment of exponents occurring in power laws. We have illustrated our model by adapting and applying it to the analysis of polydispersity effects in the self-diffusion coefficient study of Leger et al.[2] and find that the effects of polydispersity take an entirely different form from that assumed in their original analysis. Although our final correction to the self-diffusion exponent is small (see eq 3.38), our model shows that this is a consequence of the low rate of polydispersity variation rather than the low polydispersities employed by Leger et al. This conclusion is not obvious from the outset, since in spite of the low polydispersities, we find that the computed decay curves are distinctly nonexponential (see eq 3.30 and Figure 2). The single-exponential approximation only *appears* to fit the observed intensity decay, owing to the background levels used in the fitting function $S_{\text{fit}}(t)$. For this reason, a new interpretation of the least-squares fitting procedure employed by Leger et al. was required (see section IIIC). Additionally, although the observed polydispersities are overestimated by GPC measurements, the rate of variation in polydispersity is much less affected by this kind of error. Our main results are independent of both the precise polydispersities of the samples and the assumed form of molecular weight distribution.

More generally, our model establishes a method of properly understanding and accurately evaluating the effects of polydispersity in any experiment where the type of molecular weight averaging modifying the measured quantities is known. In the experiments similar to that of Leger et al., our analysis already provides a more realistic and easily calculable model for the decay of the average scattering amplitude of the excitation pattern.

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Appendix A

The number-averaged grating amplitude $\langle A_{\mathbf{q},M}(t)\rangle$, discussed in section III, is given in terms of dimensionless quantities by eq 3.28. In this appendix we show how to evaluate this integral by the Gaussian approximation for both the log-normal and Schulz model molecular weight distributions.

For the log-normal model, the dimensionless number distribution $\tilde{n}_P(m)$ is given in Table I. We convert the semiinfinite interval of integration in eq 3.28 to an infinite interval by the change of variable $y \equiv \ln (mP^{1/2})$. This gives

$$\langle A_{\mathbf{q},M}(t)\rangle = [\beta(\pi)^{1/2}]^{-1} \int_{-\infty}^{\infty} \exp[-f(y)]\, \mathrm{d}y \qquad \text{(A.1)}$$

where the exponent is

$$f(y) = \mu \exp(-yx) + (y + \tfrac{1}{2}\beta^2)^2/\beta^2 \qquad \text{(A.2)}$$

We have also defined

$$\mu = P^{x/2}\tilde{t} \qquad \text{(A.3)}$$

and

$$\beta = (2 \ln P)^{1/2} \qquad \text{(A.4)}$$

The Gaussian approximation consists of making a Taylor expansion about the stationary point of the exponent. In the present case, $f(y)$ has a single minimum at the solution y_0 of the equation

$$f'(y_0) = -x\mu \exp(-y_0x) + 2y_0/\beta^2 + 1 = 0 \qquad \text{(A.5)}$$

Using the Taylor expansion carried to second order at y_0, we then have

$$\langle A_{\mathbf{q},M}(t)\rangle \simeq [\beta(\pi)^{1/2}]^{-1} \int_{-\infty}^{\infty} \exp[-f(y_0) - \tfrac{1}{2}f''(y_0) \times (y - y_0)^2]\, \mathrm{d}y = \{\beta \exp[f(y_0)][\tfrac{1}{2}f''(y_0)]^{1/2}\}^{-1} \qquad \text{(A.6)}$$

When $f(y_0)$ and $f''(y_0)$ are evaluated from eq A.2 and μ is eliminated via eq A.5, this finally becomes

$$\langle A_{\mathbf{q},M}(t)\rangle \simeq \frac{\exp[-(2y_0/\beta^2 + 1)\{x^{-1} + \tfrac{1}{4}\beta^2(2y_0/\beta^2 + 1)\}]}{[1 + \tfrac{1}{2}x\beta^2(2y_0/\beta^2 + 1)]^{1/2}} \qquad \text{(A.7)}$$

The Schulz model is treated the same way. With the number distribution given in Table I and the change of variable $y \equiv \ln [(b + 2)m]$, where b is related to the polydispersity by $b = (P + 1)/(P + 2)$, we obtain

$$\langle A_{\mathbf{q},M}(t)\rangle = \Gamma(b + 1)^{-1} \int_{-\infty}^{\infty} \exp[-f(y)]\, \mathrm{d}y \qquad \text{(A.8)}$$

The exponent is now

$$f(y) = (b + 2)^x\tilde{t} \exp(-yx) - (b + 1)y + \exp(y) \qquad \text{(A.9)}$$

The saddle point method then gives

$$\langle A_{\mathbf{q},M}(t)\rangle \simeq \frac{\pi^{1/2} \exp[(b + 1)(x^{-1} + y_0) - (x^{-1} + 1)e^{y_0}]}{\Gamma(b + 1)[\tfrac{1}{2}\{(x + 1)e^{y_0} - x(b + 1)\}]^{1/2}} \qquad \text{(A.10)}$$

where y_0 is the solution of

$$f'(y_0) = -x(b + 2)^x\tilde{t} \exp(-y_0x) - (b + 1) + \exp(y_0) = 0 \qquad \text{(A.11)}$$

We have tested the accuracy of this method by comparison with the results of exact numerical integration. The corrections were negligible for the polydispersities $P = 1.06 \rightarrow 1.12$ encountered in the experiment of Leger et al.

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Expansion of a Polymer Chain in a Θ Solvent: The Screened-Interaction Model

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ABSTRACT: The model develops the assumption that in the Θ state the chain self-repulsion due to the covolume is exactly balanced by a free energy attraction influenced by the solvent (Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303). It is shown that if the balance is exact for two atoms remote along the chain, the interaction between closer atoms is repulsive because the maximum of the a priori probability for their distance r tends to concentrate in the covolume-forbidden region around $r = 0$. As a consequence, an expansion over the ideal size of the phantom chain appears, which develops in a range roughly between 10 and 1000 chain atoms, and asymptotically tends to a constant value for large molecular weights. Considering a realistic estimate of the van der Waals size of the chain atoms and assuming a Gaussian distribution for their mutual distance, with a suitable lower cutoff to account for the non-Gaussian behavior of short-chain sections ($\lesssim$40–60 skeletal atoms), the resulting mean-square expansion is about 5%, 20%, and 30% for polyethylene, atactic polystyrene, and isotactic polypropylene, respectively.

The Model

Several years ago in a fundamental paper[1] Flory showed that the free energy A of a dissolved polymer molecule may be expressed as follows:

$$(A - A_0)/k_BT = {}^3\!/_2(\alpha^2 - 1) - 3 \ln \alpha + a_2(\alpha) \quad (1)$$

where A_0 is the free energy of the ideal phantom chain, α is the degree of expansion assumed as uniform, and $a_2(\alpha)$, proportional to α^{-3}, is essentially the second virial term; i.e., it depends on the probability of pairwise contacts between chain atoms. Both in a Θ solution and in the melt the a_2 term vanishes and the chain behaves ideally, i.e., $\alpha = 1$; however, while in the molten state this result proceeds from the mixing entropy of very long chains tending to zero, it is quite a different matter for an ideal solution, where a small, positive solvent–polymer energy interaction exactly compensates the negative entropic term.[1,2] The resulting situation may also be viewed in terms of polymer segment–segment interactions alone, neglecting explicit reference to the solvent, by stating that the expansion effect due to the intrinsic volume of the chain is balanced by the (solvent influenced) attraction between the polymer segments.[2]

In the present paper we will further develop the logical implications of the above picture. It was shown recently through a perturbative approach applied to the expanded chain configurations (thereby ignoring higher order correlations among intrachain contacts) that $a_2(\alpha)$ may be expressed as[3]

$$a_2(\alpha) = \sum_{k<m}\sum a_2\{k,m\} = \beta \sum_{k<m}\sum W_{km}(0) \quad (2)$$

where $W_{km}(\mathbf{r})$ is the probability density for the vector distance r between the kth and the mth chain atoms and β is the excluded volume parameter. It should be stressed that we refer to the actual probability for the real chain—as opposed to that for the unperturbed, phantom chain—which opens the way to a self-consistent type of configurational description.[3] A more general formulation of the above result is

$$a_2(\alpha) = \sum_{k<m}\sum \int_V e(\mathbf{r}) W_{km}(\mathbf{r})\, d^3\mathbf{r} \quad (3)$$

where $k_BTe(\mathbf{r})$ is the effective interaction free energy function between two chain atoms;[4] this is sufficiently short-ranged for many purposes that $e(\mathbf{r}) \simeq \beta\delta(\mathbf{r})$ ($\delta(\mathbf{r})$ is the Dirac δ function in three dimensions), so that eq 2 is recovered. In terms of the classical perturbative approach (see, in particular, eq 13.1 and 13.2 of ref 4) the effective potential function $e(\mathbf{r})$ may be written as

$$e(\mathbf{r}) = 1 - \exp(-w(\mathbf{r})/k_BT) \; (=-\chi(r)) \quad (4)$$

where $w(\mathbf{r})$ represents the actual potential for a pairwise interaction. Such a potential will be considered as effectively renormalized to include the higher order interactions involving atoms in the vicinity of those two on which the pairwise interaction is based, according to the ideas of Khokhlov.[5]

It will be useful henceforth to distinguish two contributions within the function $e(\mathbf{r})$, respectively corresponding to the *covolume* and to the *solvent interaction* effect. While the former merely prohibits the spatial self-interference of the chain, the latter effect accounts for the free energy difference between a polymer self-contact and the polymer–solvent interactions that would take place in its absence. Since here we assume the size of the solvent molecules to be small, an interaction will be regarded as localized around any chain atom in a region of space of about the same size as that of a statistical segment of the polymer. Accordingly, for two chain atoms at a distance r we have

$$e(\mathbf{r}) = e_c(\mathbf{r}) + e_{si}(\mathbf{r}) \quad (5)$$

Although both the covolume (e_c) and the solvent-interaction (e_{si}) functions are short-ranged, the latter obviously survives at larger r's; since it is related with the dis-

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