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Polymer Localization by Random Fixed Impurities: Gaussian Chains

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ABSTRACT: Simple dimensional analysis is employed to discuss the relevance of impurity interactions on the molecular dimensions of flexible polymers in the limits of high- and low-impurity densities. Scaling arguments account for the universal behavior of static properties observed by Baumgärtner and Muthukumar in their recent Monte Carlo simulations. An approximate model of the random impurity interaction is introduced by considering the random impurities as being analogous to an "effective surface" with which the polymer interacts. Qualitatively the same conclusions are obtained as in the scaling arguments except that the effective surface analogy provides closed form scaling functions describing the variation of the molecular dimensions as a function of the dimensionless disorder interaction. The transition to a collapsed state is found to be characterized by a critical impurity density which is a function of the chain length.

1. Introduction

Recently, Baumgärtner and Muthukumar[1] (MB) investigated the configurational properties of a polymer in an array of randomly distributed fixed obstacles ("impurities") and found a crossover from random coil to "collapsed" chain configurations with an increasing impurity concentration. For the idealized random walk model that they consider, the limiting collapsed chain dimensions are found to be independent of chain length and dependent in a universal way on the impurity concentration.

A close quantum mechanical analogue of this problem, the scattering of an electron in an array of randomly distributed impurity centers, has been studied extensively over the last 30 years, and this formalism can be transcribed with little variation to the polymer problem.[2-12] The polymer collapse transition due to impurities in a quantum mechanical context corresponds to a change from a free-electron (conducting) state to a localized (nonconducting) state with increasing impurity concentration. Calculations by Edwards[8,10] using the path integral formulation of the one-electron Green's function averaged over random impurities indicate that this transition occurs because the randomly distributed impurities generate a net attractive interaction, giving rise to the localization transition for sufficient disorder. MB give the same interpretation to the polymer collapse due to a net effective attractive interaction generated by impurities.[1] Edwards and others have also noted the close mathematical analogy between electron localization and polymer collapse due to binary self-attractive excluded volume interactions.[8,10,13]

2. The Model

Following the standard model[2-12] for impurity interacting electrons, MB introduce the impurity-averaged end-to-end vector distribution function for the polymer as

$$\langle G(\mathbf{R},0;N)\rangle = \int \mathrm{d}\mathbf{R}_\alpha\, P(\mathbf{R}_\alpha) \int_{\mathbf{R}(0)=0}^{\mathbf{R}(N)=\mathbf{R}} D[\mathbf{R}(\tau)]\, \exp(-H/K_\mathrm{B}T) \qquad (2.1\mathrm{a})$$

$$H/K_\mathrm{B}T = H_0 + H_\mathrm{I} \qquad (2.1\mathrm{b})$$

$$H_0 = (d/2l) \int_0^N \mathrm{d}\tau\, |\mathrm{d}\mathbf{R}(\tau)/\mathrm{d}\tau|^2$$

$$H_\mathrm{I} = (\beta^0{}_\mathrm{p}/l) \sum_{\alpha=1}^{N_\mathrm{I}} \int_0^N \mathrm{d}\tau\, \delta[\mathbf{R}(\tau) - \mathbf{R}_\alpha] \qquad (2.1\mathrm{c})$$

where N_I is the number of impurities in the system at positions $\mathbf{R}_\alpha$ and $\beta^0{}_\mathrm{p}$ is a coupling constant for the point impurity–polymer interaction. $P(\mathbf{R}_\alpha)$ describes the distribution of impurities which is taken to be random in the simulation of MB. Other choices of $P(\mathbf{R}_\alpha)$ are of course possible, and $\beta^0{}_\mathrm{p}$ can be more generally taken as a random variable as well. The variable N is the chain length, d is the dimension, l is the Kuhn length, and τ is the contour distance measured along the chain. In the analogue quantum mechanical problem, N is replaced by imaginary time, the dimension d by electron mass, and the Kuhn length l by Plank's constant $\hbar$. See ref 2, 3, and 10 for a detailed discussion of the impurity-averaging formalism and the quantum mechanical analogue of (2.1) corresponding to the average propagator for an electron moving in a background of fixed random scatterers.

Below we introduce dimensionless units for the position vectors of the impurities and polymer chain, $\mathbf{R}_\alpha$ and $\mathbf{R}(\tau)$, respectively, and the chain length $N = nl$ as

$$\mathbf{R}(x)(d/\langle\mathbf{R}^2\rangle_0)^{1/2} = \mathbf{r}(x)$$

$$\mathbf{R}_\alpha(d/\langle\mathbf{R}^2\rangle_0)^{1/2} = \mathbf{r}_\alpha \qquad x = \tau/N \qquad (2.2)$$

The Hamiltonian $H/K_\mathrm{B}T$ in these units is equal to

$$H_0 = (1/2)\int_0^1 \mathrm{d}x\, |\mathrm{d}\mathbf{r}(x)/\mathrm{d}x|^2$$

$$H_\mathrm{I} = \beta^0{}_\mathrm{p}(d/2\pi l^2)^{d/2} n^{1-d/2} \sum_{\alpha=1}^{N_\mathrm{I}} \int_0^1 \mathrm{d}x\, (2\pi)^{d/2}\delta[\mathbf{r}(x) - \mathbf{r}_\alpha] \qquad (2.3)$$

These reduced units are helpful in the dimensional analysis arguments introduced below.

3. Vanishing Impurity Concentration Limit

The effect of impurities depends very much on their concentration and distribution in space. In the limit of a vanishing concentration, where few impurities are in the proximity of the chain, we can take $P(\mathbf{R}_\alpha)$ as a sum of few δ function interactions at isolated points. For illustration, consider a single "impurity" situated at the origin,

$$P(\mathbf{R}_\alpha) = \delta(\mathbf{R}_\alpha) \qquad (3.1)$$

Inserting (3.1) into (2.1) reduces the impurity Hamiltonian to

$$H/K_BT = H_0 + z^0{}_p \int_0^1 \delta[\mathbf{r}(x)](2\pi)^{d/2}\,dx \qquad (3.2a)$$

$$z^0{}_p = (d/2\pi l^2)^{d/2}\beta^0{}_p n^{\phi_p} \qquad \phi_p \equiv (2-d)/2 \qquad (3.2b)$$

which is studied in detail by Douglas et al.[14] Equation 3.2 is useful for discussing some of the qualitative effects of impurities in the low-concentration limit.

The critical dimension in the case of a repulsive polymer–impurity interaction is determined by the vanishing of the crossover exponent ϕ_p in (3.2a). It is evident that $d = 2$ is the critical dimension for a single repulsive point impurity. Addition of several impurities to the proximity to the chain should leave this conclusion unchanged. The practical implication of this observation can be seen from the explicit calculations of Douglas et al.[14] where the mean square end-to-end distance $\langle \mathbf{R}^2 \rangle$ of a single impurity interacting chain equals ($d = 3$)

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0\{1 + 2z^0{}_p + \mathcal{O}[(z^0{}_p)^2]\} \qquad (3.3a)$$

$$z^0{}_p(d = 3) = (3/2\pi l^2)^{3/2}\beta^0{}_p n^{-1/2} \qquad (3.3b)$$

where the chain has one of its ends at the origin. In the limit of infinite chains, we have $z^0{}_p \rightarrow 0$ for finite-impurity interaction $\beta^0{}_p$ and $\langle \mathbf{R}^2 \rangle$ approaches its unperturbed value $\langle \mathbf{R}^2 \rangle_0$. This is the usual situation for an "irrelevant" interaction (i.e., d above the critical dimension of the interaction). Simple dimensional analysis is not appropriate for classifying interactions when attractive interactions are involved, however. This point is underlined by the exact lattice calculations of Rubin[15] for the collapse of a polymer onto an attractive point in three dimensions. One can hardly classify an interaction which brings about the collapse of the polymer as being "irrelevant"! The same consideration applies to the collapse transition from attractive self-interaction of the chain.[16]

Before proceeding to the opposite extreme of a high concentration of impurities, it is useful to reiterate the qualitative effect of impurities at *low concentration.* A repulsive polymer–impurity interaction increases the chain dimensions albeit to a degree which decreases with increasing chain length in $d = 3$, while an attractive interaction causes a contraction of the chain and eventually chain collapse.

4. High-Impurity-Concentration Limit

The usual situation of a polymer in solution can be thought of as corresponding to the limit of an infinite concentration of impurities where the solvent molecules are taken as the impurities. It is implicit in the application of the two-parameter model that the solvent uniformly fills space (no density fluctuations) so that the solvent degrees of freedom can be "integrated out" to yield[16,17] the usual two-parameter model Hamiltonian given by

$$H(\text{excluded volume})/K_BT = H_0 + H_{EV} \qquad (4.1)$$

$$H_{EV} = z^0{}_2 \int_0^1 dx \int_0^1 dx'\, \delta[\mathbf{r}(x) - \mathbf{r}(x')](2\pi)^{d/2} \qquad (4.2a)$$

$$z^0{}_2 = (d/2\pi l^2)^{d/2}\beta^0{}_2 n^{\phi_2} \qquad \phi_2 = (4-d)/2 \qquad (4.2b)$$

where $\beta^0{}_2$ is the excluded volume binary cluster and $z^0{}_2$ the standard Fixman parameter.[16,17] The delta function in (4.2a) is a coarse-grained model of the true potential of the mean interaction determined at a microscopic level by a complex interplay of polymer–polymer, polymer–solvent, and solvent–solvent interactions.[16,17] The Hamiltonian (4.2a) may be considered a particular example of the impurity Hamiltonian (2.3), where $\mathbf{r}_\alpha$ is the chain position vector $\mathbf{r}(x)$. Observe that averaging over $\mathbf{r}_\alpha$ changes the dependence of the dimensionless interaction on chain length (i.e., the exponent ϕ). Further examples of this occurrence are described in ref 14 where the $\mathbf{r}_\alpha$'s are taken to be Euclidean surfaces of different dimensions.

For high- but finite-impurity concentrations, where there are fluctuations in the density of the space occupied by the polymer, various situations can arise intermediate between the idealized vanishing and infinite-impurity-concentration limits. An especially interesting situation is the case of randomly distributed impurities. Calcualtion for this case follows standard calculational procedures[2-12] for the density of states of an electron in a random potential array with minor variation since different properties need to be calculated in the analogue polymer problem.

Following Edward's analysis[19] in the case of the random point impurities, it is found that the effective Hamiltonian, obtained after averaging over the random impurity degrees of freedom, is characterized by a dimensionless polymer–impurity interaction,

$$z^0{}_I = (d/2\pi l^2)^{d/2}\beta^0{}_I n^{\phi_2} \qquad \phi_2 = (4-d)/2 \qquad (4.3a)$$

which scales with chain length in the same way as the Fixman parameter [see (4.2)] for excluded volume.[16-19] Very importantly, the impurity interaction coupling constant $\beta^0{}_I$ for the averaged interaction is proportional to the impurity density ρ and the *square* of the impurity–polymer interaction so that we have[19]

$$\beta^0{}_I \propto -(\beta^0{}_p)^2\rho \qquad (4.3b)$$

As a consequence, the impurity interactions (attractive or repulsive) always induce a net attractive interaction which causes the polymer to contract. This situation is contrasted with the few impurity limit considered in section 3. Addition of repulsive polymer excluded volume interactions will, of course, counterbalance this contraction, but this complication will be avoided in the present paper. The same scaling relation (eq 4.3b) between the random impurity coupling constant, $\beta^0{}_I$, the density, ρ, and the point interaction coupling constant, $\beta^0{}_p$, is found in the analogue electron localization problem.[10,11] Application of the random impurity Hamiltonian is limited to the high density and weak interaction limit specified by the condition that $\beta^0{}_I$ remains finite even though ρ is large.[3,9-12]

Following MB, we can take the impurity density, ρ, as proportional to $(1 - p)$, with p being the "porosity" (see MB for details of the definition of p), and this yields

$$z^0{}_I(d = 3) \propto (1 - p)n^{1/2} \qquad (4.4)$$

for a constant point–impurity interaction, $\beta^0{}_p$, as in the MB simulations. Good evidence that (4.4) is the universal scaling variable appropriate to the lattice simulations is provided by MB.

5. Random Impurity Induced Collapse

Muthukumar and Edwards[19] have made preliminary calculations based on the effective Hamiltonian for the random impurity model following methods closely analogous to Feynman's treatment of the polaron problem (see ref 11). Since these results will be discussed elsewhere, there is no point in discussing this calculation in detail here. It is only noted that these calculations indicate that $\langle \mathbf{R}^2 \rangle$ for a large impurity interaction (i.e., $|z^0{}_\mathrm{I}| \gg 1$) approaches ($d = 3$)

$$\langle \mathbf{R}^2 \rangle \sim |\beta^0{}_\mathrm{I}|^{-2} \tag{5.1}$$

which is independent of molecular weight. Combining (4.3), (4.4), and (5.1), we have in the limiting collapsed regime

$$\langle \mathbf{R}^2 \rangle \sim (1 - p)^{-2} \tag{5.2}$$

which is in accord with the Monte Carlo simulations of MB. The calculations of Muthukumar and Edwards for the polymer–random impurity problem are straightforward aside from the formal use of replica methods. Until these formal manipulations are carefully checked, however, the calculations must be considered as tentative.[19] At present we can be encouraged that analytic and simulation calculations lead to consistent results.

Although an exact calculation for the random impurity problem is not attempted here, we can readily understand the qualitative results of Muthukumar and Edwards and the numerical results of MB through a simple scaling argument. This scaling argument is followed by another approximate approach which yields predictions for the full scaling functions as a function of $z^0{}_\mathrm{I}$ in the random impurity problem.

There are two relevant length scales in the problem of a collapsing polymer—the unperturbed dimensions, $\langle \mathbf{R}^2 \rangle_0{}^{1/2}$, and a correlation length, ξ, characterizing the dimensions of the collapsed coil. For an impurity induced collapse transition, there should be an extensive change in the free energy, ΔF, reflecting the reduction in the chain local degrees of freedom. This implies that $\Delta F/K_\mathrm{B}T \sim n$, and by dimensonal consistency we have

$$\Delta F/K_\mathrm{B}T \sim \langle \mathbf{R}^2 \rangle_0/\xi^2 \tag{5.3}$$

Furthermore, consistency with the scaling of the dimensionless disorder interaction, $z^0{}_\mathrm{I}$ requires

$$\Delta F/K_\mathrm{B}T \sim n \sim |z^0{}_\mathrm{I}|^{2/\epsilon}, \qquad \epsilon = 4 - d \tag{5.4}$$

and (5.3) and (5.4) imply

$$\xi^2 \sim \langle \mathbf{R}^2 \rangle_0 |z^0{}_\mathrm{I}|^{-2/\epsilon}, \qquad |z^0{}_\mathrm{I}| \gg 1 \tag{5.5}$$

Using the definition of $z^0{}_\mathrm{I}$ in (4.3a) implies that (5.5) reduces to (5.1) for $d = 3$, and a new prediction here is that the exponent in (5.1) changes to unity for two dimensions. In three dimensions, (5.5) and (4.4) give for the mean dimensions of the chain

$$\xi = (1 - p)^{-1} \tag{5.6}$$

with the prefactor molecular weight independent as found in the simulations of MB and the preliminary calculations by Muthukumar and Edwards.[19]

Similar reasoning to (5.3)–(5.5) leads to a corresponding exact result for a polymer absorbed on a surface (see ref 14), and this observation forms the basis of a more complete treatment of the problem below. It is also notable that (5.4) [with $z^0{}_\mathrm{I}$ replaced by $z^0{}_2$ in (4.2b)] is consistent with Monte Carlo data for the free energy of a polymer collapsing from self-attractive interactions.[20] Further, Gaylord and Douglas[21] employ the argument (5.3)–(5.5) in a simple but rather successful model of rubber elasticity which accounts for the "localization" of the Gaussian network chain where the surrounding network chains play the role of $\mathbf{R}_\alpha$ in (2.1c). de Gennes[22] first pointed out the connection between electron localization and the localization of a network chain in rubber and also popularized the "tube model" of such localized chains.

Another approximate approach considered here is to model the many-body effective Hamiltonian of the random impurity problem by a dimensionally consistent approximate Hamiltonian. To achieve this, we visualize the background of random impurities as forming a field of random dust in which the chain is embedded. Douglas et al.[14] recently presented exact calculations for a polymer interacting with surfaces having continuously variable dimension over the whole range of surface interaction (attraction and repulsion). From these calculations, it was found that the expansion of a block within an AB diblock copolymer of repelling Gaussian chains could be understood semiquantitatively by comparison with the analogous problem of a surface interacting polymer, where one of the blocks in this analogy is taken as a surface of fractal dimension 2 appropriate for Gaussian chains.[23-25] It seems worthwhile to test this type of analogy further by modeling the background impurities in a similar fashion.

The Hamiltonian for a polymer interacting with a surface of variable dimension $d_\parallel$ is given by

$$H/K_\mathrm{B}T = H_0 + z^0{}_\mathrm{s} \int_0^1 \delta[\mathbf{r}_\perp(x)](2\pi)^{-d_\perp/2} \tag{5.7a}$$

$$z^0{}_\mathrm{s} = (d/2\pi l^2)^{d_\perp/2} \beta^0{}_\mathrm{s} n^{\phi_\mathrm{s}} \qquad \phi_\mathrm{s} = \epsilon_\perp/2$$
$$\epsilon_\perp = 2 + d_\parallel - d \tag{5.7b}$$

where $\mathbf{r}_\perp(x)$ is the projection of the position vector $\mathbf{r}(x)$ onto the $d_\perp$ dimensional space orthogonal to the interacting surface of dimension $d_\parallel$, and $\beta^0{}_\mathrm{s}$ is the surface interaction coupling constant. Equation 5.7 reduces to (3.2) in the limit $d_\parallel \to 0$. We obtain consistency of the dimensionless interactions in (5.7b) and (4.3a) by taking $d_\parallel$ equal to two (corresponding to a random fractal dust of dimension 2[26]) and by identifying $\mathbf{r}_\perp(x)$ with the position vector of the interacting chain and $\beta^0{}_\mathrm{s}$ with $\beta^0{}_\mathrm{I}$. From the exact calculations of Douglas et al.[14] we immediately obtain a prediction for the crossover scaling functions describing many of the properties of interest. For example, from (3.7e) of ref 14, the end-to-end distance is equal to

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_0 \{ \sum_{K=0}^{\infty} (-1)^K [z^0{}_\mathrm{I} \Gamma(\epsilon/2)]^K / \Gamma(2 + K\epsilon/2) \}/Q \tag{5.8a}$$

$$Q = \sum_{m=0}^{\infty} [-z^0{}_\mathrm{I} \Gamma(\epsilon/2)]^m / \Gamma(1 + m\epsilon/2) \qquad \epsilon = 4 - d \tag{5.8b}$$

It is shown in Douglas et al. that $\langle \mathbf{R}^2 \rangle$ in (5.8) has the asymptotic behavior,

$$\langle \mathbf{R}^2 \rangle \sim \langle \mathbf{R}^2 \rangle_0 |z^0{}_\mathrm{I}|^{-2/\epsilon} \qquad z^0{}_\mathrm{I} < 0, \quad |z^0{}_\mathrm{I}| \gg 1 \tag{5.9}$$

as argued for in (5.5) and found in the preliminary calculations of Muthukumar and Edwards.[19] An interesting qualitative feature predicted by (5.8) is that the collapse transition occurs for a critical value of the disorder interaction,[27]

$$z^0{}_\mathrm{I} \sim \text{constant} \tag{5.10}$$

corresponding to a density, ρ, of impurities scaling as [see (4.3a)]

$$\rho_\mathrm{c} \sim n^{-\epsilon/2}/(\beta^0{}_\mathrm{p})^2 \tag{5.11}$$

The critical density, ρ_c, thus decreases with increasing chain length and polymer–impurity interaction. However, if the polymer–impurity interaction, $\beta^0{}_p$, is small, corresponding to a relative transparency of the polymer to the impurities, the critical density required to induce concentration is higher.

Equation 5.8 gives a unique description of the crossover function for the full range of disorder, $z^0{}_I$, which can be compared with the results of the type given by MB. Numerous other properties are given in Douglas et al.,[14] which could be employed in a comprehensive comparison between theory and Monte Carlo data to test the correspondence suggested above. A similar analogy known as the Potential Well Approximation has been exploited by Economou[28] in a successful approximate model of electron localization in disordered materials.

6. Conclusions

Scaling arguments and a simple model are introduced to describe the collapse transition observed by Baumgärtner and Muthukumar in their Monte Carlo simulations of random walks interacting with random fixed impurities. It is found that the observed data have a rather simple interpretation using concepts familiar to the theory of polymer adsorption and the theory of electron localization. A universal scaling function is proposed to describe the mean molecular dimensions of impurity interacting chains without excluded volume. A subsequent paper will focus on the additional effect of polymer–polymer excluded volume in conjunction with the impurity interaction.

There are important motivations for studying the random impurity problem beyond the practical applications already mentioned by MB.[1] The paradigm of effective attractive interactions generated by random density fluctuations in the medium surrounding the polymer provides a new perspective for understanding some of the most basic polymer solution properties. For example, it is difficult to understand on the basis of the usual two-parameter model of excluded volume why polymers frequently exhibit an upper critical solution temperature above which the molecular dimensions of the chain begin to *contract*. Chu et al.[29] have recently studied this phenomenon in detail and observed that many polymers exhibit two distinct θ temperatures, θ_U and θ_L, below which and above which, respectively, the chain undergoes gradual contraction. For intermediate temperatures $\theta_U \leq T \leq \theta_L$, the chain dimensions have extended random coil or swollen configurations. In some cases, it is observed that θ_U and θ_L are so close that an intermediate good solvent regime does not even exist.[29] Chu et al. also make the interesting observation that θ_L is typically near the critical point of the pure solvent.

Now Chu et al.'s observations are contrasted with the predictions of the two-parameter theory. For simplicity of discussion, consider $z^0{}_2$ to have the mean field dependence on temperature ($d = 3$)

$$z^0{}_2 \sim [(T - \theta)/T]n^{1/2} \tag{6.1}$$

predicted by Flory (see ref 16). The expected result from (6.1) is that as the temperature is increased $z^0{}_2$ gradually approaches a maximum value for a given chain length corresponding to a maximum expansion of the chain.

The conflict between the two-parameter model and the observed data of Chu et al.[29] can be rationalized by first noting that near the solvent critical point we should expect density fluctuations in the solvent. The two-parameter model treats the solvent as a continuous medium, so it is not surprising that this model (or even the Flory lattice model[30]) has difficulties in explaining the existence of a lower critical solution temperature. Now if we consider the density fluctuations of the solvent as being impurities whose density grows with increasing temperature (i.e., as the critical point of the pure solvent is approached), then the polymer collapse with increasing temperature could be seen as a kind of localization transition due to random impurities. Of course the discussion here is a bit speculative and is meant only to suggest a new way of thinking about the problem.

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(18) It might seem tempting to conclude from (4.3) that the disorder interaction had a critical dimension of 4 corresponding to the vanishing of ϕ_2, and one might naively try to utilize renormalization group methods in conjunction with ϵ-expansion methods ($\epsilon = 4 - d$) to treat polymer localization. Many efforts along this line have been made in the context of electron localization by random impurities where it is found that such a procedure is *not possible*. For a discussion on this point see: (a) Edwards, S. F.; Green, M. B.; Srinivasan, G. *Philos. Mag.* **1977**, *355*, 1421. (b) Reference 13. (c) Nitzan, A.; Freed, K. F.; Cohen, M. H. *Phys. Rev. B: Solid State* **1977**, *15*, 4476. The basic conclusion obtained from naively treating the impurity problem with the RG-ϵ expansion method is that there is no stable fixed point—a result common to many problems where random impurity averaging is involved. A review of the difficulties obtained in viewing the localization transition from the perspective of field theory is given by: Parisi, G. *J. Phys. A* **1981**, *14*, 735. For a recent discussion of the issue of the critical dimension in the electron localization (Anderson localization) problem see: Castellani, C.; DiCastro, C.; Peliti, L. *J. Phys. A* **1986**, *19*, L 1099. Castellani et al. conclude that the upper critical dimension of the random impurity problem is infinity. This is consistent with the discussion in section 3 of this paper for the single attractive impurity problem. If you turn up the attractive interaction far enough, eventually there will be localization ("collapse") regardless of the dimension. Consequently, there should be no finite upper critical dimension in the random impurity model. Moreover, the same reasoning implies that there should be no upper critical dimension in the polymer collapse problem in contrast to the prediction that $d = 4$ is its upper critical dimension: Moore, M. A. *J. Phys. A* **1977**, *10*, 305.

(19) Edwards, S. F., unpublished notes. Edwards suggests that his formal replica calculations for a polymer in an array of fixed random impurities should be considered with caution until carefully checked. A generalization to d dimensions of Edwards' calculation by the author yields a result consistent with (5.5) and (5.9). Edwards (*Physica A: (Amsterdam)* **1979**, *96A*, 212) discusses the differences between the averaging for fixed ("quenched") random impurities versus free ("annealed") random impurities. According to Edwards' calculation, the relatively simple case of free random impurities interacting through a δ function polymer–point interaction corresponds to an effective Hamiltonian given by (4.1) and (4.2) with $z^0{}_{\mathrm{I}}$ replacing $z^0{}_2$ in (4.2b). The main effect of free impurities for chains with excluded volume should be to simply *shift* (obviously true within perturbation theory) the binary interaction to an effective one, $z_2(\mathrm{eff}) = (d/2\pi l^2)^{d/2}(\beta^0{}_2 - \beta^0{}_{\mathrm{I}})n^{\epsilon/2}$. Thus, when free impurities are introduced, to a good solvent, the polymer dimensions should decrease until a critical density, ρ^*, is reached where $z_2(\mathrm{eff}) = 0$ and an effective θ point is achieved. The compensation point critical density, ρ^*, is given by $\rho^* \sim \beta^0{}_2/(\beta^0{}_{\mathrm{p}})^2$. Recent calculations by D. Thirumalai (*Phys. Rev. A* **1988**, *37*, 269) yield the results for $z_2(\mathrm{eff})$ and ρ^* indicated above where the excluded volume (repulsive interactions only) is not restricted to be small. Thirumalai's calculation is based on Edwards–Singh (*J. Chem. Soc., Faraday Trans. 2* **1979**, *73*, 100) renormalized perturbation theory. If we accept that random free impurities simply renormalize z_2, then polymer collapse of chains with excluded volume should occur for chains at impurity densities higher than ρ^* corresponding to the limit $z_2(\mathrm{eff}) \sim -u^*{}_2$, $u^*{}_2 = \epsilon/8 + 0\ (\epsilon^2)$. See ref 14 and Douglas and Freed (*Macromolecules* **1985**, *18*, 2445). The author plans to discuss polymer collapse due to impurities for chains with excluded volume in a future publication. While the present paper was in the process of review, the author became aware of a preprint by M. J. Muthukumar and S. F. Edwards ("The Size of the Polymer in Random Media". submitted for publication in *J. Chem. Phys.*) giving a presentation of the replica calculation of $\langle \mathbf{R}^2 \rangle$ for a chain with fixed random impurities mentioned above.

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(22) De Gennes, P. G. *J. Phys. (Les Ulis, Fr.)* **1974**, *35*, L-133.

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(25) Douglas, J. F.; Nemirovsky, A. M.; Freed, K. F. *Macromolecules* **1986**, *19*, 2041.

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(27) The adsorption and collapse thresholds are characterized by "critical conditions" similar to (5.10) (see ref 14), and in all cases the constant in (5.10) is related to the renormalization group fixed point of the respective interaction. The author reformulated the surface-interacting chain model in terms of integral equations (submitted manuscript) to investigate the meaning of this type of instability condition and found that the RG fixed point is related to an eigenvalue of an associated homogeneous integral equation, and the instability condition can be understood on the basis of the Fredholm alternative. This approach allows for a transparent interpretation of the runaway fixed-point behavior mentioned in ref 18.

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Holographic Grating Studies of the Diffusion Process of Camphorquinone in Polycarbonate above and below T_g

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ABSTRACT: A laser-induced holographic grating relaxation study of camphorquinone in amorphous poly(bisphenol A carbonate) is carried out. For the first time it is found that, by changing the temperature, two types of line shape associated with the relaxation of the multiple grating effect can be observed. The temperature dependence of the diffusion coefficient of camphorquinone follows the LWF equation, with the LWF coefficient C_2 in agreement with the dielectric relaxation data, thus suggesting that the same type of segmental motion is responsible for diffusion and dielectric relaxation. A rapid drop of the diffusion coefficient is observed as the temperature traverses across T_g from above. Below T_g, the diffusion rate is found to decrease very slowly with decreasing temperature.

Introduction

Laser-induced holographic grating relaxation (LIHGR) is a sensitive and selective method for the measurement of tracer diffusion coefficients for photochemically labeled molecules.[1] From the shape of the time-dependent diffraction signal it has been found that multiple gratings are a common feature in the LIHGR experiment.[2,3] Multiple gratings must always be present because photoexcitation