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Isolated polymer molecule in a random environment

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The shape of a polymer molecule in the presence of randomly distributed stationary impurities is investigated using the path-integral formulation. The polymer molecule is assumed to be described by the Edwards minimal model. Calculation of the mean-square end-to-end displacement $\langle R^2\rangle$ shows that at a critical density of the scatterers the polymer molecule makes a transition from a swollen state (chain with excluded-volume interactions) to a disordered, random coiled state (a Gaussian chain). At this density there is a crossover in the value of the exponent ν (in three dimensions), characterizing the scaling of $\langle R^2\rangle$, with the length of the polymer from about 0.6 (corresponding to the excluded-volume regime) to 0.5 (corresponding to the coiled state). For densities below the critical density, the exponent ν is well described by the Flory value.

I. INTRODUCTION

The excluded-volume problem for an isolated polymer molecule, introduced by Flory, has been extensively solved by both analytical as well as numerical methods.[1] Recently, there has been considerable effort in understanding the behavior of the self-avoiding random walk on randomly diluted lattices.[2-8] These studies address the question of the effect of quenched randomness on the polymer molecule. In this paper, however, we consider the problem of the shape of an isolated polymer molecule in the presence of random scatterers in equilibrium with the polymer. Thus calculations can be done with the averaged partition function (or equivalently the observables can be calculated using averaged propagators) and thus we are explicitly dealing with an annealed system. The initial motivation for this came from experiments on DNA molecules, which showed that the DNA molecule can undergo a collapse transition when a critical amount of salt solution (or a smaller polymer molecule) is added.[9-11] These systems are annealed in the sense that the added polymer, whose density fluctuations are assumed to provide the randomness, is in equilibrium with the DNA molecule. Thus, it is of interest to consider the effect of annealed randomness on the shape of polymers. Although the model sketched here does not have any obvious relevance to the aforementioned class of experiments, we feel that the theory provided here may be general enough to attempt a microscopic calculation of the collapse transition.

The extremely idealized model we study is the following. An isolated polymer molecule is allowed to interact with stationary impurities which are distributed at random. The interaction potential between the polymer segment (a bead-spring model is assumed) and the impurities is taken to be short-ranged and weak. The question of interest is the effect of the random scatterers on the shape of the polymer molecule as the density of impurities is changed. One can anticipate the answer to this question by generalizing the well-known intuitive argument of Lifshitz[12] in the context of the calculation of the density of states in electronically disordered systems.[13,14] This argument for the present problem can be summarized as follows. The polymer molecule would rather be in a region free of the random scatterers. When the density of scatterers is sufficiently low, this is indeed possible and any occasional cost in energy due to the overlap of the polymer segment with the impurities is easily compensated by the gain in avoiding the intramolecular contact. The probability of finding a region, $\Omega=(4\pi/3)\langle R^2\rangle^{3/2}$, is proportional to $e^{-\rho\Omega}$. As ρ increases, however, this probability becomes smaller and the segments of the polymers overlap considerably with the scatterers. This suggests that there should exist a critical density where the potential of interaction between the polymer and the scatterers is not compensated by the intramolecular interaction. At this critical density the polymer undergoes a transition from the swollen state to a random coiled state. From these plausible arguments it appears that this transition is entropically driven. Unlike the case of the calculation of electronic energy levels in disordered systems, where the Lifshitz arguments can be used to obtain the functional form of the density of low-lying energy levels, it does not appear easy to compute the critical density in terms of the fundamental parameters of the Hamiltonian. This can, however, be accomplished by using path-integral methods and this is the major purpose of this paper. In particular, we use a self-consistent first-order perturbation theory to calculate the value of the critical density in terms of the basic parameters of the Edwards minimal model. Some of the analytical results can be obtained without performing the calculations in a manner presented here. The main advantage of doing this is that the structure of the theory becomes more transparent and the extension to higher orders can be carried out using the results presented in the Appendix.

The organization of the paper is as follows. In Sec. II the model is described in detail. The calculation of $\langle R^2\rangle$ is also given in Sec. II. Section III is devoted to the calculation of distribution of the end-to-end vectors, $P(R,L)$, and the changes in this function at the critical density are described. The paper is concluded in Sec. IV with a discussion and some speculations concerning the possibility of observing similar behavior in tethered surfaces. The relevant formulas that have been utilized in obtaining the results are derived in the Appendix.

II. THEORY

A. The model

We will use the continuum model for the polymer, which not only proves to be convenient for the analysis but is also quite accurate in predicting certain static properties. The dimensionless "Hamiltonian" for the isolated polymer molecule is assumed to be of the form, first proposed by Edwards,[14,15] namely,

$$H(r(s))=\frac{3}{2l}\int_0^L \dot{r}^2(s)\,ds +\omega\int_0^L ds\int_0^L ds'\,\delta(r(s)-r(s'))\ . \quad (2.1)$$

The conformation of the polymer is given by the continuous curve $r(s)$ in d dimensions and is parametrized by the variable s. When $\omega=0$, the Hamiltonian corresponds to a completely flexible Gaussian chain with l the Kuhn length. The mean-square end-to-end distance $\langle R^2\rangle$ for such a chain is easily obtained and it is given by

$$\langle R^2\rangle = Ll\ . \quad (2.2)$$

When ω (the strength of the excluded-volume interaction) is nonzero, the calculation of $\langle R^2\rangle$ can only be done by approximate methods. The approximate theories all yield the result

$$\langle R^2\rangle \sim L^{2\nu}\ , \quad (2.3)$$

where $\nu\sim 3/(d+2)$.

To describe the effect of the random scatterers we consider the discrete version of the Gaussian chain. This can be written as

$$H_D=\frac{3P}{2lL}\sum_{i=1}^{P}(r_{i+1}-r_i)^2\ , \quad (2.4)$$

and this describes a set of beads interacting by a harmonic potential with the appropriate spring constant. We assume that the interaction potential between the polymer molecule and the random scatterers can be written as

$$u[\{r_t\},\{R\}]=\sum_{t=1}^{P}\sum_{i=1}^{N}v(r_t-R_i)\ , \quad (2.5)$$

where R_i is the coordinate of the ith scatterer. In the continuum limit the contribution to the action arising from Eq. (2.5) becomes

$$u[r(s),\{R_i\}]=\sum_{i=1}^{N}\int_0^L v[r(s)-R_i]ds\ . \quad (2.6)$$

Thus, the total dimensionless action for a given realization of the environment is

$$H=\frac{3}{2l}\int_0^L \dot{r}^2(s)\,ds+\omega\int_0^L ds\int_0^L ds'\,\delta(r(s)-r(s')) +\sum_{i=1}^{N}\int_0^L v[r(s)-R_i]ds\ . \quad (2.7)$$

Thus, for each arrangement of the scatterers one can evaluate any observable which becomes a random variable, and the average value of the observable is obtained by integrating the value over the probability distribution of the random stationary scatterers. In particular, the average "partition function" may be obtained as

$$\langle Z\rangle_{\rm imp}=\int D(r(s))\exp\left[-\frac{3}{2l}\int_0^L \dot{r}^2(s)\,ds-\omega\int_0^L ds\int_0^L ds'\,\delta[r(s)-r(s')]\right]\left\langle \exp-\int_0^L u[r(s),\{R_i\}]ds\right\rangle_{\rm imp}\ . \quad (2.8)$$

The impurities are assumed to be uniformly distributed and thus the indicated averaging can be easily done. This yields in the limit $N\to\infty$, $V\to\infty$, and $N/V=\rho=$const (where V is the volume of the system and ρ is the density of scatterers),

$$\left\langle \exp-\int_0^L u[r(s),\{R_i\}]ds\right\rangle=\prod_{j=1}^{N}\int\frac{1}{V}\left[\exp-\int_0^L v[r(s)-R_i]ds\right]\frac{dR_i}{V}$$

$$=\left\{1-\int\frac{dR_i}{V}\left[1-\exp\left[-\int_0^L v[r(s)-R_i]ds\right]\right]\right\}^N$$

$$=\exp\left\{-\rho\int dR_s\left[1-\exp\left[-\int_0^L v[r(s)-R_s]ds\right]\right]\right\}\ . \quad (2.9)$$

The above formula was obtained in the context of the path-integral formulation of an electron in the presence of random scatterers.[13,16] Substituting Eq. (2.9) into (2.8) enables one to define the effective action for the problem as

$$\langle Z(\omega,\rho,L)\rangle = \int D(r(s))e^{-S(r(s))} , \tag{2.10a}$$

$$\begin{aligned} S(r(s)) = {} & \frac{3}{2l}\int_0^L \dot{r}^2(s)\,ds \\ & +\omega\int_0^L ds\int_0^L ds'\,\delta(r(s)-r(s')) \\ & +\rho\int dR_s\left[1-\exp\left[-\int_0^L ds\, v[r(s)-R_s]\right]\right] . \end{aligned} \tag{2.10b}$$

It should be noted that the problem of an electron in a random potential is usually described in terms of the action in Eq. (2.10b) with $\omega=0$. In fact, using the resulting action as a model for electronically disordered systems, Friedburg and Luttinger[13] were able to calculate the Lifshitz tail (as well as the first corrections) by evaluating $\langle Z(\omega=0,\rho,L\to\infty)\rangle$ and then performing the required inverse Laplace transform. This completes the description of the action to be considered in this article and we will calculate average properties like the mean-square end-to-end displacement $\langle R^2\rangle$ and the shape of the distribution function $P(R,L)$. All averages are obtained with respect to the action S,

$$\langle f\rangle = \frac{\int D(r(s))fe^{-S(r(s))}}{\int D(r(s))e^{-S(r(s))}} . \tag{2.11}$$

So far the precise form for $v(r-R_i)$ has not been specified. For the present problem, we assume that $v(r-R_i)$ is given by a contact potential of the form

$$v(r-R_i) = \beta v_0\delta(r-R_i)/l . \tag{2.12}$$

We have divided $v(r-R_i)$ by the Kuhn length l for dimensional purposes. Such a factor would not exist if the length of the polymer were described by the number of monomer units instead of L. If one wants to capture the qualitative physics of the situations discussed in the Introduction (like the collapse transition in DNA), one has to consider other more realistic forms for $v(r-R_i)$. These will be pursued elsewhere.

B. Mean-square end-to-end distance

For the polymer molecules described by the action given by Eq. (2.10b), with the potential of interaction between the segment of the polymer given by Eq. (2.12), we calculate the mean-square end-to-end distance $\langle R^2\rangle$ given by

$$\langle R^2\rangle = \frac{\int D(r(s))\,|r(L)-r(0)|^2\exp[-S(r(s))]}{\int D(r(s))\exp[-S(r(s))]} . \tag{2.13}$$

In order to evaluate the above path integral, we employ the self-consistent variational approach introduced by Edwards and Singh.[17,18] Their procedure lies in choosing an effective reference action with an appropriately renormalized step length l_1 such that $\langle R^2\rangle = Ll_1$. The quantity l_1 satisfies a self-consistent equation, and for the model considered here l_1 is a function of l, ω, ρ, and L. The equation satisfied by l_1 is obtained by insisting that all corrections to the relation $\langle R^2\rangle \equiv Ll_1$ be identically zero. Thus, following Edwards and Singh, we choose the reference action to be[19]

$$S_0 = \frac{3}{2l_1}\int_0^L \dot{r}^2(s)\,ds , \tag{2.14}$$

and this implies that $\langle R^2\rangle \equiv Ll_1$. The action for our problem may be written as

$$\begin{aligned} S &= S_0+S-S_0 \\ &= \frac{3}{2l_1}\int_0^L \dot{r}^2(s)\,\mathrm{ds}+B , \end{aligned} \tag{2.15a}$$

where $B\equiv B_1+B_2+B_3$ and

$$B_1 = \frac{3}{2}\left[\frac{1}{l}-\frac{1}{l_1}\right]\int_0^L \dot{r}^2(s)\,ds , \tag{2.15b}$$

$$B_2 = \omega\int_0^L ds\int_0^L ds'\,\delta[r(s)r(s')] , \tag{2.15c}$$

$$B_3 = \rho\int dR_s\left[1-\exp\left[-\int_0^L v[r(s)-R_s]\right]\right] . \tag{2.15d}$$

With this $\langle R^2\rangle$ becomes

$$\begin{aligned} \langle R^2\rangle = {} & Ll_1+[\langle B\rangle\langle\,|r(L)r(0)|^2\rangle-\langle B\,|r(L)-r(0)|^2\rangle] \\ & +\left[\left\langle\frac{B^2}{2}\left|r(L)-r(0)\right|^2\right\rangle-\langle B\rangle\langle B\,|r(L)-r(0)|^2\rangle-\left\langle\frac{B^2}{2}\right\rangle\langle\,|r(L)-r(0)|^2\rangle\right]+\cdots . \end{aligned} \tag{2.16}$$

The averages indicated in Eq. (2.18) are with respect to the reference action S_0.

Thus, if l_1 is chosen such that $\langle R^2\rangle = Ll_1$, then to first order in B, a self-consistent equation for l_1 is obtained from the equation

$$\begin{aligned} & \int B\exp[-S_0(r(s))]D(r(s))\int\,|r(L)-r(0)|^2\exp[-S_0(r(s))]D(r(s)) \\ & \qquad = \int\,|r(L)-r(0)|^2B\exp[-S_0(r(s))]D(r(s)) . \end{aligned} \tag{2.17}$$

The evaluation of the path integrals appearing in the above equation is presented in the Appendix. Using these results the self-consistent equation for l_1 is seen to satisfy

$$Ll_1^2\left[\frac{1}{l}-\frac{1}{l_1}\right]=2\omega\left[\frac{6}{\pi^3}\right]^{1/2}\frac{L^{3/2}}{l_1^{1/2}}-2\rho\left[\frac{\beta v_0}{l}\right]^2\left[\frac{6}{\pi^3}\right]^{1/2}\frac{L^{3/2}}{l_1^{1/2}} . \tag{2.18}$$

Note that for $\rho=0$, Eq. (2.18) reduces to the result obtained by Edwards and Singh. When the density is small or when $\omega L^{1/2}\rightarrow\infty$, then

$$l_1\sim L^{1/5} , \tag{2.19}$$

which, when substituted into the right-hand side of Eq. (2.16) yields the familiar Flory result

$$\langle R^2\rangle\sim L^{6/5}\ (d=3) . \tag{2.20}$$

Equation (2.18) also suggests the existence of a critical density ρ^* given by

$$\rho^*=\omega\left[\frac{l}{\beta v_0}\right]^2 , \tag{2.21}$$

at which there is a crossover for the exponent characterizing the excluded volume limit ($\nu=\frac{3}{5}$) to the Gaussian or disordered, coiled limit ($\nu=\frac{1}{2}$). This is precisely the behavior that was predicted on an intuitive basis by generalizing the familiar Lifshitz argument used in electronically disordered systems. It is interesting that the crossover behavior should be observed regardless of the length of the polymer. However, the very existence of Eq. (2.18) assumes perturbation which is only valid when one considers large polymers.

III. DISTRIBUTION FUNCTION

In this section we derive the probability distribution function $P(R,L)$ using the formalism outlined in Sec. II. The distribution function $P(\mathbf{R},L)$ is given by

$$P(\mathbf{R},L)=\langle\delta[\mathbf{R}-r(\mathbf{L})-r(0)]\rangle \tag{3.1a}$$

and may be written as

$$P(\mathbf{R},L)=N_0^{-1}\int\frac{d^3K}{(2\pi)^3}\int D(r(s))\times\exp\left[i\mathbf{K}\cdot\int_0^L\dot r(s)-S(r(s))\right] , \tag{3.1b}$$

where

$$N_0=\int D(r(s))\exp\{-S[r(s)]\} .$$

The strategy used in evaluating $P(\mathbf{R},L)$ is the same as above, i.e., we use a reference action and calculate a perturbative correction to $P(\mathbf{R},L)$ and the parameters of the reference action are chosen so that all the corrections are made to vanish. Just as in Sec. II we will present a first-order perturbative calculation which yields the desired self-consistent equation for l_1. As indicated later, the essential result of this section can be obtained without adopting the Edwards-Singh procedure.[17,18] However, the general structure of the theory becomes transparent with this procedure. It proves convenient to consider[17] $Q(\lambda,L)$,

$$Q(\lambda,L)=N_0^{-1}\int D(r(s))\exp[\lambda\int_0^L\dot r(s)-S(r(s))] , \tag{3.2}$$

with λ real. This yields convergent quantities and the $P(K,L)$ can be obtained by straightforward analytic continuation.

Following exactly the steps outlined in Sec. II, we can write Eq. (3.2) as an expansion in powers of B [cf. Eq. (2.16)],

$$\begin{aligned}Q(\lambda,L)=&N_0^{-1}\left\langle\exp\left[\lambda\int_0^L\dot r(u)\,du\right]\right\rangle\\&+\left[N_0^{-1}\left\langle\exp\left[\lambda\int_0^L\dot r(u)\,du\right]B\right\rangle-N_0^{-2}\langle B\rangle\left\langle\exp\left[\lambda\int_0^L\dot r(u)\,du\right]\right\rangle\right]\\&+O(B^2) .\end{aligned} \tag{3.3}$$

The indicated averages in Eq. (3.3) are done with respect to the action given in Eq. (2.14). The evaluation of the first term in Eq. (3.3) gives

$$N_0^{-1}\left\langle\exp\left[\lambda\int_0^L\dot r(u)\,du\right]\right\rangle=\left[\frac{3}{2\pi lL}\right]^{3/2}e^{\lambda^2Ll_1/6} . \tag{3.4}$$

To order (B^2), the self-consistent equation for l_1 is obtained by setting the expression in square brackets in Eq. (3.3) to zero, namely,

$$N_0^{-1}\left\langle B\exp\left[\lambda\int_0^L\dot r(u)\,du\right]\right\rangle=N_0^{-2}\langle B\rangle\left\langle\exp\left[\lambda\int_0^L\dot r(u)\,du\right]\right\rangle . \tag{3.5}$$

The averages indicated in Eq. (3.5) are quite similar to those encountered in the Appendix. Using these averages, the desired self-consistent equation for l_1 is obtained from Eq. (3.5) as,

$$\frac{\lambda^2 l_1 L}{6}\left(\frac{1}{l}-\frac{1}{l_1}\right)=\left[\frac{3}{4}\left(\frac{6}{\pi^3}\right)^{1/2}\frac{\omega L^{1/2}}{l_1^{3/2}}-\frac{3}{4}\rho\left(\frac{\beta v_0}{l}\right)^2\left(\frac{6}{\pi^3}\right)^{1/2}\frac{L^{1/2}}{l_1^{3/2}}\right]\times\int_0^1 ds\frac{1-\exp(-\lambda^2 l_1 L\sigma/6)}{\sigma^{3/2}}\ . \tag{3.6}$$

When the density is zero, then Eq. (3.6) reduces to that found by Edwards and Singh. We now consider the case when the ρ is less than the critical density. Following Edwards and Singh, we consider the more interesting case when $\lambda^2 L l_1$ is large. Equation (3.6) becomes

$$\left(\frac{\lambda^2 L l_1^2}{6l}\right)=\frac{3}{4}\left(\frac{6}{\pi^3}\right)^{1/2} y\int_0^1 d\sigma\frac{(1-e^{-\lambda^2 L l_1\sigma/6})}{\sigma^{3/2}}\ , \tag{3.7a}$$

where

$$y=\left[\omega-\rho\left(\frac{\beta v_0}{l}\right)^2\right]\frac{L^{1/2}}{l_1^{3/2}}\ . \tag{3.7b}$$

By letting $t^2=\lambda^2 L l_1\sigma/6$, in Eq. (3.7a) one can obtain an equation for l_1 as

$$l_1=\left(\frac{9}{\pi}\right)^{1/3}\left(\frac{\Delta l}{\lambda}\right)^{1/2}, \tag{3.8a}$$

where

$$\Delta=\left[\omega-\rho\left(\frac{\beta v_0}{l}\right)^2\right]. \tag{3.8b}$$

As stated in the Appendix, the evaluation of the contribution to the effective action from the random impurities has been considered only to second order in v_0. To this order, Eq. (3.8) suggests that the only effect is an effective reduction in the excluded-volume interaction. It should be emphasized that this result can be easily obtained by expanding Eq. (2.15b) in powers of v_0 and performing the resulting R_s integral without resorting to the Edwards-Singh formalism. The reason we have followed the latter approach is to establish that the formalism of Edwards and Singh can be utilized for problems of the sort posed here. More importantly, to the order this calculation has been carried out, it can be shown that if one includes terms $O(B^2)$, $O(B^3)$, etc. [where B is given by Eq. (2.15a)], then the structure of Eq. (3.9) remains unaltered and only the numerical coefficient gets changed. This is most clearly seen within the context of the Edwards-Singh formalism.[17]

One can immediately write $Q(\lambda)$ as

$$Q(\lambda)=\exp(\lambda^2 L l_1/6)=\exp\left[\lambda^{5/3}\left(\frac{9l\Delta}{\pi}\right)^{1/3}L/6\right]. \tag{3.9}$$

Thus the probability distribution function becomes

$$P(R,L)\sim\int d^3K\exp[(iK)^{5/3}(9l\Delta/\pi)^{1/3}L/6-i\mathbf{K}\cdot\mathbf{R}]\ . \tag{3.10}$$

The K integral can be evaluated by the method of steepest descents and this yields[20,21]

$$P(R,L)\sim\exp\left[-\left(\frac{18}{5}\right)^{3/2}\frac{\sqrt{\pi}}{3}\left(\frac{R^2}{\Delta^{2/5}l^{2/5}L^{6/5}}\right)^{5/4}\right]+O(1/L)\ . \tag{3.11}$$

For ρ less than the critical density, one sees that $P(R,L)$ is more sharply peaked than compared to the case without the random scatterers. At the critical density the self-consistent solution for l_1 yields exactly

$$l_1=l\ , \tag{3.12a}$$

and consequently

$$P(R,L)\sim\exp(-3R^2/2Ll)\ . \tag{3.12b}$$

It follows that for long polymers at the critical density there is a crossover from the behavior given by Eq. (3.11) to the distribution function characteristic of the Gaussian chain. This observation could have been predicted from the results of Sec. II but an explicit calculation also demonstrates this. For the case when $\lambda^2 L l_1$ is small[17] we merely quote the results. Below the critical density the behavior of $P(R,L)$ is also Gaussian except that the dispersion is

$$\sigma^2=(2)^{2/5}(6/\pi^3)^{1/5}\omega^{2/5}L^{6/5}l^{2/5}$$

and at the critical density $P(R,L)$ remains a Gaussian but σ^2 given by Eq. (3.12).

IV. CONCLUSIONS

We conclude this paper with the following remarks.

(1) In this paper we have considered the statistics of a linear polymer in the presence of a random environment. The randomness is assumed to be annealed and this allows us to calculate observables from average propagators. We have shown, at least to within first-order perturbation theory, that at a critical density of the random scatterers the exponent ν characterizing the mean-square end-to-end distance exhibits a crossover from the excluded-volume behavior to the random coiled behavior. A similar crossover is found for the probability of the end-to-end distance distribution function. The physical arguments lead one to assert that the results should be valid in general, even beyond perturbation theory.

(2) It appears that the predictions of this theory can be tested by experimental measurements. It is known that[22,23] one can use cross-linking techniques to trap a polymer molecule in a random network composed of micronodules. This has been done by using a mixture of

two chains and cross-linking[24] one at a later stage. Apparently one also achieves this by adding a polymer molecule to a block copolymer. The thermodynamic conditions may be adjusted to trap the polymer in a random network. The applicability of the theory outlined here rests on the fundamental assumption that one can perform annealed averages. However, it is possible these situations may require the need to perform quenched averages, a problem which is considerably more difficult.

(3) Recently, Kantor *et al.*[25] have proposed that two-dimensional surfaces of fixed connectivity embedded in three dimensions could be a caricature for a number of physically interesting examples. Based on the results presented here, it is tempting to speculate that the conformations of tethered surfaces in the presence of impurities could undergo a considerable reduction in size, as measured by the radius of gyration. The theory for such a problem can be set up by generalizing the action given in Eq. (2.1b), i.e.,

$$S(r(\mathbf{x}))=\frac{3}{2l^2}\int d^2\mathbf{x}\,\dot{r}^{\,2}(\mathbf{x})+\omega\int_0^L d^2\mathbf{x}\int_0^L d^2\mathbf{x}'\delta(r(\mathbf{x})-r(x'))+\rho\int dR_s\left[1-\exp\left[-\int_0^L v[r(\mathbf{x})-l_s]d^2\mathbf{x}\right]\right]. \tag{4.1}$$

Following Kantor *et al.* or using the procedure utilized here, the conformations of the tethered surface for the above theory can be calculated. This calculation will be presented elsewhere.

(4) There is considerable theoretical interest in studying the effect of quenched random impurities on the shape of the polymer molecule.[2-8] There is evidently a good deal of contradiction in these results. Based on a Monte Carlo simulation, Kremer[2] suggested that the exponent ν (describing the scaling of the mean-square end-to-end distance with the number of monomer units constituting the polymer molecule) is unaffected as long as one is below the percolation threshold. At the percolation threshold, it is argued that ν changes to $\frac{2}{3}$, which is higher than the Flory swelling exponent. Rammal *et al.*[6] have argued that dilution should definitely affect ν at least at the percolation threshold. These results seem to be in conflict with the Harris criteria[26] and, indeed, Harris[5] has argued that quenched disorder should be irrelevant (in the renormalization-group sense) for the polymer problem. In particular, there should be no modification of the exponent ν and it should coincide with the pure case value. For the continuum model presented here the configurational average of the logarithm of the generating functional can be carried using the replica trick. A preliminary analysis[27] of the resulting theory suggests that it has the form found in the mean-field theory of dilute spin glasses.[28]

(5) The calculations have been done by including the effect of random impurities to second order in v_0. In fact, one can assess the effect of including higher-order terms in v_0 in evaluating α_3 [cf. Eq. (A2c)]. It is known that fourth- and higher-order terms in v_0 (which after integrating over the impurity coordinate R_s act as four-body and higher-body interaction terms) can be ignored because the correction to $\langle R^2\rangle$ from these terms are of the order of $L^{-1/2}$ (Ref. 29). Thus one needs to include only the term proportional to v_0^3. The calculation can be performed using the formulas given in the Appendix and in the limit of $l \ll L$; the self-consistent equation for l_1 is

$$\alpha^5-\alpha^3=\frac{4}{3}\left[\frac{3}{2\pi}\right]^{3/2}\frac{L^{1/2}}{l^{3/2}}\Delta+\frac{A}{6}\left[\frac{\beta v_0}{l}\right]^3\frac{\rho}{\alpha^3}\,, \tag{4.2}$$

where $\alpha^2=l_1/l$ is the swelling ratio Δ given by Eq. (3.8b), and A is a numerical coefficient given by[30]

$$A=2\left[\frac{3}{2\pi}\right]^3\frac{1}{6}\times\int_0^1 dx\int_0^1 dx'\int_0^1 dx''\frac{(x-x'')}{[(x-x')(x'-x'')]^{3/2}}\,. \tag{4.3}$$

Analysis of Eq. (4.2) proceeds along the same lines outlined elsewhere.[9,10,30] Specifically, as long as $t=(A/6)(\beta v_0/l)^3\rho$ is less than a critical value, the transition density given by Eq. (2.21) remains unchanged. Furthermore, the transition from a swollen state to a random coiled state is sharp. When t is greater than a critical value then the polymer molecule contracts smoothly as ρ approaches ρ^*. Thus, the conclusions drawn in this paper remain valid even when higher-order terms are considered.

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APPENDIX

In this appendix we describe the evaluation of the path integrals occurring in Eq. (2.17). The calculation of the other crucial equations in the rest of the paper may be accomplished using the formulas presented here. Since the right-hand side of Eq. (2.17) is more complicated than the left-hand side we will consider it first,

$$\int D(r(s))\,|\,r(L)-r(0)\,|^{2B}\exp\{-S_0[r(s)]\}\equiv\alpha_1+\alpha_2+\alpha_3\,, \tag{A1}$$

where

$$\alpha_1=\frac{3}{2}\left[\frac{1}{l}-\frac{1}{l_1}\right]\left\langle |r(L)-r(0)|^2\int_0^L \dot r^2(s)\,ds\right\rangle , \tag{A2a}$$

$$\alpha_2=\omega\left\langle |r(L)-r(0)|^2\int_0^L ds\int_0^L ds'\,\delta(r(s)-r(s'))\right\rangle , \tag{A2b}$$

and

$$\alpha_3=\rho\left\langle |r(L)-r(0)|^2 \times\int dR\left[1-\exp\left[-\int_0^L v[r(s)-R]\right]\right]\right\rangle . \tag{A2c}$$

The averages in Eq. (A2) are done with respect to the action in Eq. (2.14). The averages (α_1) and (α_2) have been already done by Edwards and Singh and for completeness we will indicate the steps and quote the results.

By considering the expression

$$I(x)=\frac{\int D(r(s))\,|r(L)-r(0)|^2\exp\left[x\int_0^L \dot r^2(s)\,ds\right]}{\int D(r(s))\exp\left[x\int_0^L \dot r^2(s)\,ds\right]} , \tag{A3}$$

one can write α_1 as

$$\frac{3}{2}\left[\frac{1}{l}-\frac{1}{l_1}\right]\int D(r(s))\,|r(L)-r(0)|^2\int_0^L \dot r^2(s)\,ds\,\exp\{-S_0[r(s)]\}$$

$$=\frac{3}{2}\left[\frac{1}{l}-\frac{1}{l_1}\right]I'(x)\bigg|_{x=3/2(1/l-1/l_1)}+\langle R^2\rangle\bar B_1=Ll_1^2\left[\frac{1}{l}-\frac{1}{l'}\right]+\langle R^2\rangle\bar B_1 \tag{A4}$$

with

$$\bar B_1=\frac{3}{2}\left[\frac{1}{l}-\frac{1}{l'}\right]\int D(r(s))\int_0^L \dot r^2(s)\,ds\,e^{-S_0(r(s))} . \tag{A5}$$

Equation (A2b) may be evaluated by writing α_2 as

$$\alpha_2=\frac{\omega}{(2\pi)^3}\int\int\int\int D(r(s))ds\,ds'\,d^3k\,|r(L)-r(0)|^2\exp\{-S_0(r(s))+i\mathbf{k}\cdot[\mathbf{r}(s)-\mathbf{r}(s')]\} . \tag{A6}$$

The path integral in Eq. (A6) is the propagator for a free particle subject to an impulsive external potential and is readily evaluated. The remaining integrals are computed by completing squares and the result of this straightforward calculation yields

$$\alpha_2=\frac{\omega\langle R^2\rangle}{2\pi^2}\int ds\int ds'\int_0^\infty k^2e^{-k^2|s-s'|l_1/6}dk-2\omega\left[\frac{6}{\pi^3}\right]^{1/2}\frac{L^{3/2}}{l_1^{1/2}} . \tag{A7}$$

For the choice of the interaction between the scatterer and the polymer segment given by Eq. (2.12), one can write α_3 as

$$\alpha_3=\rho\int dR_s\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n!}\left[\frac{\beta v_0}{l}\right]^n\int ds_1\cdots ds_n\int D(r(s))\,|r(L)-r(0)|^2\prod_{i=1}^{n}\delta(r(s_i)-R_s)\exp[-S_0(r(s))] . \tag{A8}$$

In order to evaluate the path integral, one needs the following propagator:

$$G(r',r,L)=\int_{r(0)=r}^{r(L)=r'}D(r(s))\int\prod_{i=1}^{n}\delta(r(s_i)-R_s)\exp\left[-\frac{3}{2l_1}\int_0^L \dot r^2(s)\,ds\right]ds_i . \tag{A9}$$

Using an integral representation of the δ function, Eq. (A9) becomes

$$G(r',r,L)=\prod_{i=1}^{n}\int\frac{d^3k_i}{(2\pi)^3}\int D(r(s))\exp\left[-\frac{3}{2l_1}\int_0^L \dot r^2(u)\,du+i\int_0^L r(u)\left[\sum_{i=1}^{n}k_i\delta(s_i-u)\right]du\right] . \tag{A10}$$

This is nothing but the propagator for a free particle subject to a sequence of impulses and can be easily calculated. The normalized propagator is

$$G(r',r;L,n)=\left[\frac{3}{2\pi l_1 L}\right]^{3/2}\exp\frac{l_1}{12}\left[\sum_{i,j}\mathbf{k}_i\cdot\mathbf{k}_j(\,|s_i-s_j|+s_is_j-2s_j)\right]$$
$$+\exp-\left[\frac{3}{2Ll_1}(r'-r)^2+i(r'-r)\left[\sum_i k_i(1-\frac{1}{L}s_i)\right]\right]. \tag{A11}$$

A special case of this formula was used in evaluating α_2. If the Green's function in Eq. (A11) is substituted in Eq. (A8) and the R_s integral is performed one gets the condition that $\delta(\sum_i k_i)$, implying that the total momentum is conserved at each vertex in the scattering process. The resulting expression for α_3 can indeed be represented in terms of Feynman diagrams for each n. Here we evaluate α_3 to second order, i.e., only terms up to $n=2$ (or of the order of v_0^2 are retained). The resulting expressions are somewhat tedious but can be easily calculated, leading to

$$\alpha_3 \simeq \rho\left[\frac{\beta v_0 L}{l}\langle R^2\rangle-\frac{1}{2}\left[\frac{\beta v_0}{l}\right]^2\int ds_1 ds_2\frac{d^3k}{(2\pi)^3}\tilde{A}(k,-k)\right], \tag{A12a}$$

where

$$\tilde{A}(k,-k)=\left[Ll_1-\frac{l_1^2k^2}{9}\right]\exp\left[-\frac{l_1k^2}{6}|s_1-s_2|\right]. \tag{A12b}$$

In a similar fashion, the evaluation of $\langle B\rangle\langle R^2\rangle$ can be calculated. Here, we simply quote the results.

$$\langle B\rangle\langle R^2\rangle=\langle R^2\rangle\langle\bar{B}_1\rangle+\frac{\omega\langle R^2\rangle}{2\pi^2}\int ds_1 ds_2 dk\, k^2 e^{-k^2|s-s'|/6}$$
$$+\rho\langle R^2\rangle\left[\frac{\beta v_0 L}{l}-\frac{1}{2}\left[\frac{\beta v_0}{l}\right]^2\right]\int\frac{ds_1 ds_2 d^3k}{(2\pi)^3}e^{-l_1k^2|s_1-s_2|/6}, \tag{A13}$$

where $\langle\bar{B}_1\rangle$ is given by Eq. (A5). Equating Eq. (A13) to the sum of α_1, α_2, and α_3 readily leads to the self-consistent equation for l_1 [see Eq. (2.18)] to first order in B.

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