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Polymer Molecules at Chemically Random Surfaces[†]

K. Sumithra and K. L. Sebastian*

Department of Applied Chemistry, Cochin University of Science and Technology, Cochin 682022, India

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We consider the adsorption of polymers on the surface of a solid, occupying the region $z < 0$. The usual approach to the problem is the one due to de Gennes. We show that the propagator of this approach can be represented in terms of path integrals, where the paths are unconstrained and can enter the region $z < 0$ too. Using this approach, we consider adsorption on a flat, but random surface—where the randomness causes the adsorption energy to be a random function of position. Using the replica trick and variational formalism, we study the size of the adsorbed polymer. To simplify the calculations, we use the ground-state dominance approximation. The calculations revealed a sudden decrease in the size of the polymer, in both the parallel and perpendicular directions, as randomness is increased beyond a certain value. Further, the size of the polymer in the perpendicular direction is found to become zero at a larger value of the randomness. To verify whether these are artifacts of the ground-state dominance approximation, we also did exact calculations for test cases. It was found that the sudden change in size was absent in the exact calculations. Increasing randomness leads to a smooth, continuous decrease in the size. Ultimately, however, the polymer was found to collapse in the perpendicular direction.

Introduction

The adsorption of polymer molecules at surfaces has been the subject of many theoretical and experimental investigations. Most of the papers concentrate on the adsorption on planar surfaces.[1-3] Long ago, Rubin[3] investigated the problem of adsorption of a single polymer chain without excluded volume on a homogeneous surface and showed that there exists a threshold energy for the adsorption of the chain. However, in almost all cases of polymer adsorption, surfaces are neither homogeneous in composition nor smooth. Although the type of heterogeneity (chemical or physical) may strongly influence the adsorption characteristics, these nonideal situations have received relatively little theoretical attention in the past,[3-5] and the processes involved are only poorly understood.

In a recent investigation, Baumgärtner and Muthukumar[4] considered the influence of both physical and chemical roughness on the adsorption of polymers using scaling arguments and Monte Carlo simulations. In this paper, we investigate analytically the problem of polymer chain adsorption at planar but chemically random surfaces. The randomness may be due to impurities on the surface or because the surface is that of an alloy, which has a random distribution of its components on the surface.

In an earlier paper,[6] we presented a short description of our approach and gave results using the ground-state dominance approximation. In this paper, we give the details, along with results of an exact evaluation of the integrals.

Adsorption on a Planar Surface: de Gennes' Approach

We first discuss the de Gennes' approach[1] to the adsorption of the polymers on a flat, uniform surface. Let $G(\vec{r},\vec{r}';N)$ be the unnormalized probability distribution function for the end vector $\vec{r}$, for a chain of length N, whose other end is at $\vec{r}'$. $G(\vec{r},\vec{r}';N)$ obeys the diffusion equation

$$\{\partial/\partial N - (1/6)\nabla^2\}G(\vec{r},\vec{r}';N) = \delta(N)\,\delta(\vec{r} - \vec{r}') \qquad (1)$$

We imagine that there is a surface at $z = 0$ and adopt the notation

$$\vec{r} = (\vec{x},z) \qquad (2)$$

The presence of the wall (surface) can lead to the attraction or repulsion of the polymer segments to it. This, according to de Gennes, may be modeled by putting

$$[\partial \ln G(\vec{r},\vec{r}';N)/\partial z]_{z=0} = -c_0 \qquad (3)$$

The sign of the constant c_0 depends on the temperature. At low temperatures, the attractive interaction between the polymer and the surface dominates, resulting in adsorption. In such cases, c_0 is positive, whereas at higher temperatures the polymer is desorbed, and correspondingly, c_0 will be negative. It is convenient to expand $G(\vec{r},\vec{r}';N)$ in terms of the eigenfunctions $\psi_m(\vec{r})$ of the problem, defined by

$$(-1/6)\nabla^2\psi_m(\vec{r}) = E_m\psi_m(\vec{r}) \qquad (4)$$

where $\psi_m(\vec{r})$ obeys

$$[\partial \ln \psi_m(\vec{r})/\partial z]_{z=0} = -c_0 \qquad (5)$$

and are normalized according to

$$\int_{z>0}\psi_m(\vec{r})\,\psi^*_m(\vec{r})\,d\vec{r} = 1 \qquad (6)$$

Then $G(\vec{r},\vec{r}';N)$ is given by

$$G(\vec{r},\vec{r}';N) = \sum\psi_m(\vec{r})\,\psi_m(\vec{r}')e^{-E_m N} \qquad (7)$$

de Gennes' prescription can easily be converted into a path integral formulation in which the paths are unconstrained and can enter the region $z < 0$ too.

Path Integral Representation for $G(\vec{r},\vec{r}';N)$. A path integral expression for $G(\vec{r},\vec{r}';N)$ is very convenient to use, in our analysis below. To arrive at such a representation, we consider $\zeta(\vec{r},\vec{r}';N)$, which corresponds to the polymer being not restricted by a hard wall but is attracted to the plane $z = 0$ by a delta function interaction. It obeys the differential equation

$$\{\partial/\partial N - (1/6)\nabla^2 - lc_0\delta(z)/3\}\zeta(\vec{r},\vec{r}';N) = \delta(N)\,\delta(\vec{r} - \vec{r}') \qquad (8)$$

and has the path integral representation

$$\zeta(\vec{r},\vec{r}';N) = \int_{\vec{r}(0)=\vec{r}'}^{\vec{r}(N)=\vec{r}} D\vec{r}(t)\,\exp[-S_\delta[\vec{r}(t)]] \qquad (9)$$

where

$$S_\delta[\vec{r}(t)] = S_0[\vec{r}(t)] - (l/3)\int_0^N c_0 \delta(z(t))\, dt \tag{10}$$

$$S_0[\vec{r}(t)] = (3/2l)\int_0^N \dot{\vec{r}}(t)^2\, dt \tag{11}$$

In Appendix A, we show that $G(\vec{r},\vec{r}';N)$ can be written as

$$G(\vec{r},\vec{r}';N) = \zeta(\vec{r},\vec{r}';N) + \zeta(P\vec{r},\vec{r}';N) \tag{12}$$

where $P\vec{r} = (\vec{x},-z)$.

Adsorption on a Random Surface

To treat adsorption on a random surface, we now generalize the approach of de Gennes and put

$$[\partial \ln G(\vec{r},\vec{r}';N)/\partial z]_{z=0} = -(c_0 + \nu(\vec{x})) \tag{13}$$

The function $\nu(\vec{x})$ is a random function of $\vec{x}$. Note that this can be used to model only variation of adsorption energy with position on the surface and would not be a model for the case where the surface is rough. An equation similar to the eq 12 is still valid and may be written as

$$G(\vec{r},\vec{r}';N) = \zeta(\vec{r},\vec{r}';N) + \zeta(P\vec{r},\vec{r}';N) \tag{14}$$

with $\zeta(\vec{r},\vec{r}';N)$ defined by

$$\zeta(\vec{r},\vec{r}';N) = \int_{\vec{r}(0)=\vec{r}'}^{\vec{r}(N)=\vec{r}} D\vec{r}(s)\, \exp\{-S_{ran}[\vec{r}(s)]\} \tag{15}$$

where

$$S_{ran}[\vec{r}(s)] = S_\delta[\vec{r}(s)] - (l/3)\int_0^N ds\, \nu(\vec{x}(s))\, \delta[z(s)] \tag{16}$$

It is quite interesting to note that the paths in the path integral in eq 15 can enter the region $z < 0$ too. To get the normalized probability distribution, we divide $G(\vec{r},\vec{r}';N)$ by $\mathcal{N}$ which is given by

$$\mathcal{N} = \int_{z>0} d\vec{r}\, G(\vec{r},\vec{r}';N) = \int d\vec{r} \int_{\vec{r}(0)=\vec{r}'}^{\vec{r}(N)=\vec{r}} D\vec{r}(s)\, \exp\{-S_{ran}[\vec{r}(s)]\} \tag{17}$$

To calculate the mean square end-to-end vector or any other average quantity, we have to perform the average over the random function $\nu(\vec{x})$. To perform this average, it is convenient to take the random function to be Gaussian with vanishing average and to have correlation function $\langle \nu(\vec{x})\,\nu(\vec{x}')\rangle = B(\vec{x} - \vec{x}')$, where $\langle ...\rangle$ denotes averaging with respect to the random function. To be specific, we consider randomness with a correlation length R_0 and take $B(\vec{x}) = V^2 \exp[-\vec{x}^2/R_0^2]$, where V is a parameter describing the strength of the randomness. Let us denote the normalized probability distribution function by $P(\vec{r},\vec{r}';N)$. It is given by

$$P(\vec{r},\vec{r}';N) = G(\vec{r},\vec{r}';N)/\mathcal{N} \tag{18}$$

$G(\vec{r},\vec{r}';N)$ is a functional of $\nu(\vec{x})$ and is still given by eq 14. The quantity of interest is $\langle P(\vec{r},\vec{r}';N)\rangle$. To calculate the average of $P(\vec{r},\vec{r}';N)$, we use the replica trick.[7] Thus we are interested in calculating $\langle \zeta(\vec{r},\vec{r}';N)/\mathcal{N}\rangle$ as $\langle P(\vec{r},\vec{r}';N)\rangle$ can be obtained from this easily. Introducing n replicas, labeled with $\alpha = 1, 2, ..., n$, one can write

$$\zeta(\vec{r},\vec{r}';N)/\mathcal{N} = \lim_{n\to 0}\prod_{\alpha=1}^n \int_{\vec{r}_\alpha(0)=\vec{r}} D\vec{r}_\alpha(s_\alpha) \times$$
$$\exp[-S_{ran}[\vec{r}_\alpha(s_\alpha)]]\delta(\vec{r}_1(N) - \vec{r}) \tag{19}$$

On performing the average over the random function $\nu(\vec{x})$

$$\langle \zeta(\vec{r},\vec{r}';N)/\mathcal{N}\rangle = \lim_{n\to 0}\left[\prod_{\alpha=1}^n \int_{\vec{r}_\alpha(0)=\vec{r}} D\vec{r}_\alpha(s_\alpha)\right] \times$$
$$\exp\{-S\}\delta[\vec{r}_1(N) - \vec{r}] \tag{20}$$

$$S = \sum_{\alpha=1}^n S_\delta[\vec{r}_\alpha(s_\alpha)] - S_1 \tag{21}$$

where S_1 is given by

$$S_1 = {}^1\!/_2[l/3]^2 \sum_{\alpha,\beta=1}^n \int_0^N ds \int_0^N dt\, B(\vec{x}_\alpha(s) - \vec{x}_\beta(t)) \times$$
$$\delta(z_\beta(t))\, \delta(z_\alpha(s)) \tag{22}$$

Our interest is only in the adsorbed molecules, for which we would like to calculate the size $\langle [\vec{r}(N) - \vec{r}(0)]^2\rangle$. The integral in eq 20 cannot be evaluated analytically. Therefore we adopt the variational formulation of Feynman's path integral technique.[8] For this we need a trial action, which should be such that all the integrals can be evaluated analytically. An action for which this can be done is

$$S_T[\vec{r}(s)] = \sum_{\alpha=1}^n S_t[\vec{r}_\alpha(s_\alpha)] \tag{23}$$

where

$$S_t[\vec{r}(s)] = S_0[\vec{r}(s)] - (lc/3)\int_0^N \delta[z(s)]\, ds +$$
$$q^2/(12lN)\int_0^N ds \int_0^N dt\, [\vec{x}(s) - \vec{x}(t)]^2 \tag{24}$$

Our action in the eq 24 has a delta function like attractive interaction with the surface. This interaction is an effective one and has no $\vec{x}$ dependence. On the other hand, there is a "harmonic oscillator"-like term depending on $\vec{x}$. It is more common to use the purely harmonic oscillator term $\int_0^N [\vec{x}(t)]^2\, dt$.[9] However, this has the defect of not being translationally invariant. Note that the action in eq 24 is separable as far as z and $\vec{x}$ coordinates are concerned. For the z direction, one has a path integral involving a Dirac delta function in its action. This can be found by changing over to the corresponding diffusion equation, which involves the operator $\{\partial/\partial N - (l/6)\partial^2/\partial z^2 - lc\delta(z)/3\}$. On the other hand, the path integral involving $\vec{x}$ may appear difficult, as it involves a nonlocal action. This also can be done easily,[10] as is demonstrated below:

Evaluation of Path Integrals Involving the Nonlocal Action. Let us consider any path integral involving the nonlocal action. We can write it as

$$I = \int_{\vec{x}(0)=\vec{x}'}^{\vec{x}(N)=\vec{x}} D\vec{x}(s)\, \exp\left[-\frac{3}{2l}\int_0^N dt \left\{\frac{d\vec{x}(t)}{dt}\right\}^2 - \right.$$
$$\left. (q^2/12lN)\int_0^N ds \int_0^N dt\, [\vec{x}(s) - \vec{x}(t)]^2\right] F[\vec{x}(s)] \tag{25}$$

In the above, $F[\vec{x}(s)]$ is any arbitrary functional of the path $\vec{x}(s)$. We now make use of the identity

$$\exp\{-(q^2/12lN)\int_0^N ds \int_0^N dt\, [\vec{x}(s) - \vec{x}(t)]^2\} =$$
$$(q^2N/6\pi l)\int d\vec{y}\, \exp\{-(q^2/6l)\int_0^N dt\, (\vec{y} - \vec{x}(t))^2\} \tag{26}$$

in eq 25 to obtain

$$I = (q^2 N/6\pi l) \int d\tilde{y} \int_{\tilde{x}(0)=\tilde{x}'}^{\tilde{x}(N)=\tilde{x}} D\tilde{x}(s) \exp\left[-\frac{3}{2l}\int^N dt \left\{\frac{d\tilde{x}(t)}{dt}\right\}^2 - (q^2/6l)\int_0^N dt \, [\tilde{x}(t) - \tilde{y}]^2\right] F[\tilde{x}(s)] \quad (27)$$

In the above equations, $\tilde{y} = (y_1, y_2)$ is a two-dimensional vector. The path integral of the eq 27 involves only a local quadratic action. Therefore, if $F[\tilde{x}(s)]$ is such that the path integral involving a local, quadratic action can be evaluated, then the one involving the nonlocal one can also be evaluated!

As a typical example, consider the following probability distribution function for the end vector $\tilde{r}$ for a polymer, whose other end is at $\tilde{r}'$, if the action were S_t. Then

$$P_t(\tilde{r},\tilde{r}';N) = I(\tilde{r},\tilde{r}';N)/\int d\tilde{r} \, I(\tilde{r},\tilde{r}';N) \quad (28)$$

where

$$I(\tilde{r},\tilde{r}';N) = \int_{\tilde{r}(0)=\tilde{r}'} D\tilde{r}(s) \exp\{-[S_t[\tilde{r}(s)]]\}\delta[\tilde{r}(N) - \tilde{r}] \quad (29)$$

Using eq 26, it is possible to write $P_t(\tilde{r},\tilde{r}';N)$ as

$$P_t(\tilde{r},\tilde{r}';N) = \int d\tilde{y} \int_{\tilde{r}(0)=\tilde{r}'}^{\tilde{r}(N)=\tilde{r}} D\tilde{r}(s) \exp(-S_t^{\tilde{y}}[\tilde{r}(s)])/$$
$$[\int d\tilde{r} \int d\tilde{y} \int_{\tilde{r}(0)=\tilde{r}'}^{\tilde{r}(N)=\tilde{r}} D\tilde{r}(s) \exp(-S_t^{\tilde{y}}[\tilde{r}(s)])] \quad (30)$$

where

$$S_t^{\tilde{y}}[\tilde{r}(s)] = S_0[\tilde{r}(s)] - (lc/3)\int_0^N \delta[z(s)] \, ds + (q^2/6l)\int_0^N ds \, [\tilde{x}(s) - \tilde{y}]^2 \quad (31)$$

The denominator in eq 30 is simply a normalization factor which ensures that $P_t(\tilde{r},\tilde{r}';N)$ is normalized. As the $\tilde{x}$ and z are not coupled in the eqs 30 and 31, one gets

$$P_t(\tilde{r},\tilde{r}';N) = I_1(\tilde{r},\tilde{r}';N)/\int d\tilde{r} \, I_1(\tilde{r},\tilde{r}';N) \quad (32)$$

with

$$I_1(\tilde{r},\tilde{r}';N) = G_\delta(z,z';N)\int d\tilde{y} \, G_{h0}^{\tilde{y}}(\tilde{x},\tilde{x}';N) \quad (33)$$

$G_\delta(z,z';N)$ is the propagator for Brownian motion in the presence of a delta function sink and obeys the differential equation

$$\{\partial/\partial N - (l/6)\partial^2/\partial z^2 - lc\delta(z)/3\}G_\delta(z,z';N) = \delta(N) \, \delta(z - z') \quad (34)$$

$G_{h0}^{\tilde{y}}(\tilde{x},\tilde{x}';N)$ is the propagator for two-dimensional Brownian motion in the presence of a parabolic sink of the form $(q^2/6l)(\tilde{x} - \tilde{y})^2$, having origin at $\tilde{y}$. It satisfies

$$\{\partial/\partial N - (l/6)\nabla_{\tilde{x}}^2 - (q^2/6l)(\tilde{x} - \tilde{y})^2\}G_{h0}^{\tilde{y}}(\tilde{x},\tilde{x}';N) = \delta(N) \, \delta(\tilde{x} - \tilde{x}') \quad (35)$$

Note that

$$G_{h0}^{\tilde{y}}(\tilde{x},\tilde{x}';N) = G_{h0}(\tilde{x}-\tilde{y},\tilde{x}'-\tilde{y};N) \quad (36)$$

where G_{h0} is the propagator corresponding to the usual harmonic oscillator action and is given by

$$G_{h0}(\tilde{x},\tilde{x}';N) = [q/2\pi l \sinh(qN/3)] \times$$
$$\exp[-(q/2l \sinh(qN/3))[\cosh(qN/3)(\tilde{x}^2 + \tilde{x}'^2) - 2\tilde{x}\tilde{x}']] \quad (37)$$

Explicit expression for $G_\delta(z,z';N)$ is available (see refs 11-13). Hence the probability $P_t(\tilde{r},\tilde{r}';N)$ is known. If $c > 0$, then the operator $-(l/6)\partial^2/\partial z^2 - lc\delta(z)/3$ has one negative eigenvalue, given by $\epsilon_b = -lc^2/6$, with the associated eigenfunction $\psi_b(z) = \sqrt{c} \exp(-c|z|)$. This corresponds to the adsorbed (bound) state of the polymer. As the paths are not restricted to the region $z > 0$, the normalization that we use is $\int_{-\infty}^{\infty} dz \, \psi_b(z)^2 = 1$. In the limit where N becomes very large, the two propagators $G_\delta(z,z';N)$ and $G_{h0}^{\tilde{y}}(\tilde{x},\tilde{x}';N)$ are dominated by the eigenfunctions having the lowest eigenvalues (ground-state dominance approximation) and one gets

$$G_\delta(z,z';N) \approx c \exp\{-c(|z| + |z'|) - \epsilon_b N\} \quad (38)$$

$$G_{h0}(\tilde{x},\tilde{x}';N) \approx (q/\pi l) \exp[-q(\tilde{x}^2 + \tilde{x}'^2)/(2l) - qN/3] \quad (39)$$

Remembering that the variational parameters c and q have to be determined so as to best suit the description of adsorbed polymers, we make use of the Feynman's variational procedure[7] for their evaluation. Thus, we expect the integral

$$I(n) = \prod_{\alpha=1}^n [\int_{\tilde{r}_\alpha(0)=\tilde{0}}^{\tilde{r}_\alpha} D\tilde{r}_\alpha(s_\alpha)] \exp[-S] \quad (40)$$

to behave like $\exp[-nF_1(N)]$ for $n \to 0$ and large N. We estimate $F_1(N)$ variationally, in the limit $n \to 0$ and choose c and q so as to get the best approximation for it. These parameters are then used to calculate $\langle [\tilde{r}(N) - \tilde{r}(0)]^2 \rangle$. So we now consider $I(n)$, and write it as

$$I(n) = [\prod_{\alpha=1}^n \int_{\tilde{r}_\alpha(0)=\tilde{0}}^{\tilde{r}_\alpha(N)=\tilde{0}} D\tilde{r}_\alpha(s_\alpha)] \exp[-S_T]\langle \exp[-(S - S_T)]\rangle_T \geq$$
$$Z_t^n \exp\langle -(S - S_T)\rangle_T \quad (41)$$

where $\langle ... \rangle_T$ denotes averaging with respect to the trial action S_T. Z_t is defined in Appendix B. Z_t and the other integrals can be evaluated analytically in the ground-state dominance approximation and hence $F_1(N)$ may be found. The integrals can also be evaluated exactly, though for some of them, one has to perform numerical integration. The details of these calculations are given in the Appendixes B and C.

Results and Discussion

Ground-State Dominance Approximation. The expression that one obtains for F_1, in the ground-state dominance approximation, written in terms of the dimensionless variables $\bar{N} = N/l$, $\bar{c} = cl$, $\bar{q} = ql$, $\bar{R}_0 = R_0/l$, $\bar{c}_0 = c_0 l$, $\bar{V} = Vl$, is

$$F_1/\bar{N} = [\bar{c}^2 - 2\bar{c}\bar{c}_0 + \bar{q} - (\bar{c}^2 2\bar{V}^2 \bar{N}\bar{R}_0^2)/\{3(2 + \bar{q}\bar{R}_0^2)(4 + \bar{q}\bar{R}_0^2)\})]/6 \quad (42)$$

Putting $\bar{u} = \bar{q}\bar{R}_0^2$, $p = 2\bar{N}\bar{V}^2/3$ and $f(\bar{u}) = p\bar{u}/[(2 + \bar{u})(6 + \bar{u})]$, we can rearrange the above equation to write an expression for $\bar{F}_1(\bar{u},\bar{c})$, defined to be equal to $6F_1/\bar{N}$ as

$$\bar{F}_1(\bar{u},\bar{c}) = [\bar{c}^2 - 2\bar{c}\bar{c}_0 + \bar{u}/\bar{R}_0^2 - \bar{c}^2 f(\bar{u})] \quad (43)$$

In eq 43, $\bar{c}^2$ represents the effect of entropy (in quantum mechanical parlance kinetic energy), trying to spread out the adsorbed chain, increasing its thickness, $-2\bar{c}\bar{c}_0$, the lowering of energy resulting from adsorption, $\bar{u}/\bar{R}_0^2$, the effect of localizing the chain to dimensions of q^{-1} in directions parallel to the surface and $-\bar{c}^2 f(\bar{u})$, the effect of the randomness, which results in a net attraction between the chains, as is indicated by the negative sign. Note that this term has $-\bar{c}^2$, because of the lowering of energy caused by adsorption. We now find the best values of $\bar{u}$ and $\bar{c}$, which make $\bar{F}_1(\bar{u},\bar{c})$ a minimum. Finding the value of $\bar{c}$

such that $\bar{F}_1(\bar{u},\bar{c})$ is a minimum gives

$$\bar{c} = \bar{c}_0/(1 - f(\bar{u})) \tag{44}$$

Note that if $\bar{c}$ is negative, there is no bound (adsorbed) state, which violates our basic assumption in deriving the eq 43. Therefore only $\bar{c} > 0$ is acceptable to us. This happens only if $f(\bar{u}) < 1$. Finding the value of $\bar{u}$ for which $f(\bar{u})$ is a maximum, one gets $\bar{u}_{max} = \sqrt{8}$. So if $f(\bar{u}_{max}) < 1$, one would never have $\bar{c} < 0$. $f(\bar{u}_{max}) < 1$ implies $p < p_0$, where $p_0 = 6 + 4\sqrt{2}$. Hence for $p > p_0$, the solution given by the eq 44 is not acceptable. The reason for this is simple. As $p \to p_0$, $\bar{c} \to \infty$; that is, the thickness of the polymer in the perpendicular direction becomes very small. If $p > p_0$, then the value of $\bar{c}$ that minimizes $\bar{F}_1(\bar{u},\bar{c})$ is ∞. That is the polymer is collapsed (has a thickness = 0) in the perpendicular direction!

Now consider $p < p_0$. For this case, we can substitute 44 into eq 43, and after some rearrangements one gets

$$(\bar{R}_0^2/\bar{N})F_1 = -(\bar{c}_0\bar{R}_0)^2 + g(\bar{u}) \tag{45}$$

where

$$g(\bar{u}) = \bar{u} - p_1\bar{u}/[(2 + \bar{u})(4 + \bar{u}) - p\bar{u}] \tag{46}$$

with $p_1 = \bar{c}_0^2\bar{R}_0^2 p$. We give in Figure 1 a plot of $g(\bar{u})$ against $\bar{u}$, for different values of p_1, for $p = 10$. If $p_1 > 8$, then the slope of the curve at $\bar{u} = 0$ is negative and there is minimum at a $\bar{u} \neq 0$. On the other hand, if $p_1 < 8$, then the slope of $g(\bar{u})$ at $\bar{u} = 0$ is positive and hence $\bar{u} = 0$ is a minimum. However there could be another, lower minimum, at a nonzero $\bar{u}$. This would happen if the $g(\bar{u})$–$\bar{u}$ plot cuts the horizontal axis for $\bar{u} > 0$. This is true for values of $p > [6 + 2(8 - p_1)^{1/2}]$, with $0 \le p_1 \le 8$. So as p crosses the value $[6 + 2(8 - p_1)^{1/2}]$, with $0 \le p_1 \le 8$, the value of $\bar{u}$ at which the minimum occurs, viz., $\bar{u}_{min}$ would change discontinuously from the value of zero to a nonzero value. These results are summarized in the Figure 2, in which we have plotted the values of $\bar{u}$ which makes $g(\bar{u})$ a minimum, viz., $\bar{u}_{min}$ against p and p_1. For $p > p_0$, the polymer is collapsed. For $p < p_0$, along the line $p = [6 + 2(8 - p_1)^{1/2}]$, with $0 \le p_1 \le 8$, the value of $\bar{u}_{min}$ changes discontinuously.

Size of the Polymer. The size of the polymer chain in the adsorbed state can be estimated using the trial action. In the z direction, the thickness of the adsorbed layer is c^{-1}. We can now use eq 28 for $P_t(\bar{r},\bar{r}';N)$ to estimate the size of the polymer molecule in the parallel direction. We find

$$\langle[\tilde{x}(N) - \tilde{x}(0)]^2\rangle/l^2 = 4\bar{R}_0^2 \tanh(\bar{u}_{min}\bar{N}/6\bar{R}_0^2)/\bar{u}_{min} \tag{47}$$

Using this equation, we arrive at the following conclusions: (1) If $p > p_0$, the polymer is collapsed in the perpendicular direction. (2) $p < p_0$: If p_1 becomes large, $\bar{u}_{min} \to \sqrt{8}$. Then, if $\sqrt{8}\bar{N}/6\bar{R}_0^2 \gg 1$, the polymer has a finite size, in the parallel direction which can be found from eq 47 to be given by

$$\langle[\tilde{x}(N) - \tilde{x}(0)]^2\rangle/l^2 = \sqrt{2}\bar{R}_0^2 \tag{48}$$

Note that this is independent of N. On the other hand, imagine that $R_0 \to \infty$. Then again, $p_1 \to \infty$, and $\bar{u}_{min} \to \sqrt{8}$. Then if $(8)^{1/2}\bar{N}/6\bar{R}_0^2 \ll 1$

$$\langle[\tilde{x}(N) - \tilde{x}(0)]^2\rangle/l^2 = 2\bar{N}/3 \tag{49}$$

and the polymer behaves like a free polymer, in the parallel direction.

Exact Calculation. We have also done a rigorous calculation of the value of $\bar{u}_{min}$ by evaluating $I_{\alpha\alpha}$ and $I_{\alpha\beta}$ exactly (see Appendix
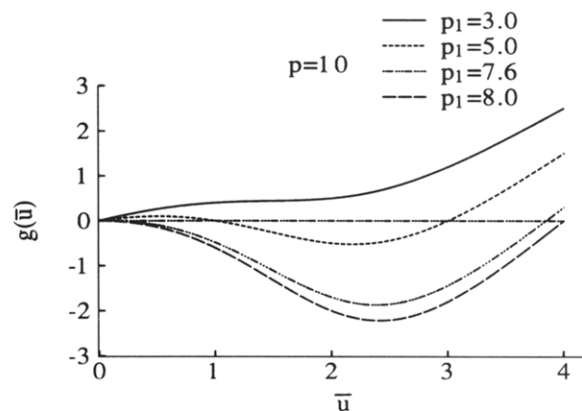

Figure 1. Plot of $g(\bar{u})$ as a function of u for different values of p_1. For $p_1 = 3$, $\bar{u}_{min} = 0$. But at $p_1 = 5$, there are two minima, with the one at $\bar{u}_{min} = 0$ not being the global minimum. For $p_1 = 8$, there is only one minimum, viz. at $\bar{u}_{min} > 0$.
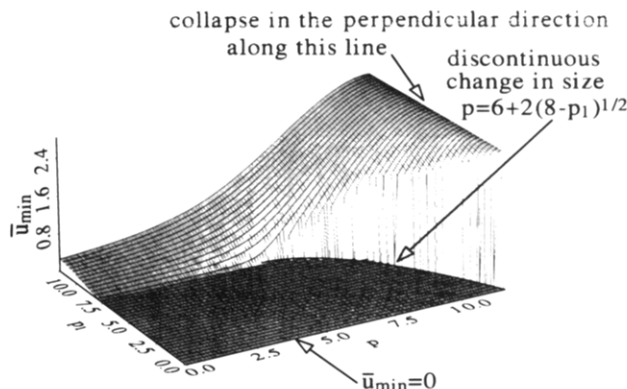

Figure 2. Plot of $\bar{u}_{min}$ for different values of p and p_1 using ground-state dominance approximation.

C for details). From the results of the appendixes we find

$$F_1 = 2 \ln\left[\frac{\sinh(\bar{g}\bar{N}/6)}{\bar{q}}\right] - (\bar{q}\bar{N}/6) \coth(\bar{q}\bar{N}/6) -$$
$$\bar{N}\bar{c}_0^2/6(1 - f(\bar{q},\bar{N})) \tag{50}$$

where

$$f(\bar{q},\bar{N}) = \bar{c}_0^2(I_{\alpha\alpha} - I_{\alpha\beta}) \tag{51}$$

In the case of calculations, using the ground-state dominance approximation, we found that there is a range of values of p and p_1 for which $\bar{u}_{min} = 0$. This means that the polymer is unaffected by the randomness. Further, $\bar{u}_{min}$ changes discontinuously along a line (see Figure 2). This means that there is a discontinuous change in the size of the polymer in the parallel and perpendicular directions. Further, there is collapse in the perpendicular direction as p exceeds p_0. To verify whether these would persist if one made an exact calculation, we took $\bar{N} = 40, 50, 60,$ and $70, \bar{c}_0 = 1$ and $\bar{R}_0 = 1$ and did an exact evaluation of $\bar{u}_{min}$, for different values of $\bar{V}$. For this case, $p = p_1 = 2\bar{N}\bar{V}^2/3$ and $\bar{u} = \bar{q}$. Changing $\bar{V}$ means that one is moving along the line $p = p_1$ in Figure 2. Simple inspection of the figure syhows that there is a discontinuous change in $\bar{u}$ ($\bar{q}$) from zero to a finite value, along this line. This is evident in the approximate results given in Figure 3 and does not occur in the exact results given in the same figure. Further, in the approximate case, for a range of values of $\bar{V}$, $\bar{u}_{min}$ is found to be zero. In contrast, the exact results always give a $\bar{u}_{min}$ which is nonzero, for $\bar{V} \neq 0$, and varies smoothly, as a function of $\bar{V}$.

This is also clear from the plots of parallel and perpendicular sizes of the polymer chain shown in Figures 4 and 5. It was also
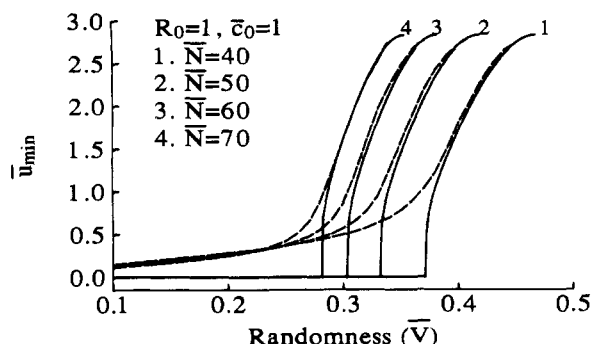
Figure 3. Plot of $\bar{u}_{min}$ as a function of randomness $(\bar{V})$ for different $\bar{N}$. The solid lines correspond to the curves for ground-state dominance approximation and the broken lines to the exact calculation.
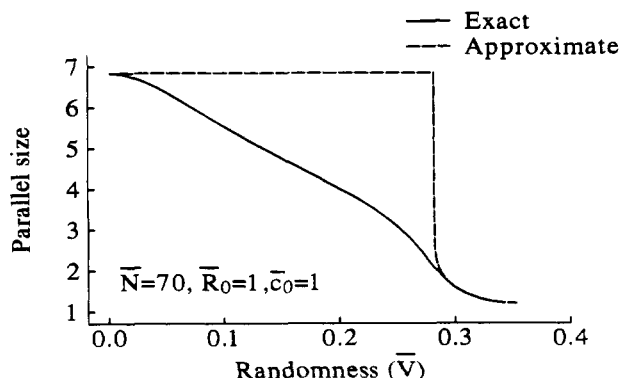

Figure 4. Plot of perpendicular size of the polymer chain, in units of l, as a function of randomness $(\bar{V})$.
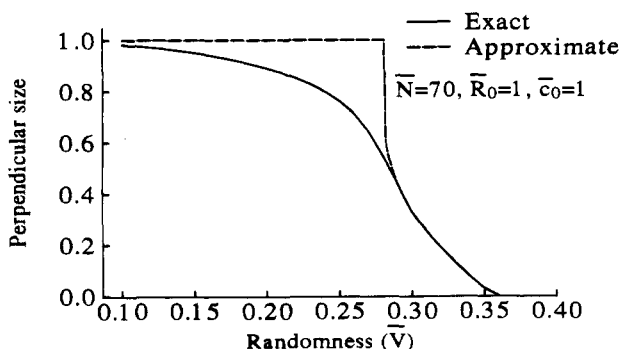

Figure 5. Plot of parallel size of the polymer chain, in units of l as a function of randomness $(\bar{V})$.

found that the collapse in the perpendicular direction occurred in the exact calculation too.

Would the inclusion of the excluded volume interaction modify the results obtained above? Muthukumar[14] has investigated a similar question for the collapse of a polymer chain in a random medium. He finds that the excluded volume interaction was screened out, and even in its presence, the collapse was present, though the actual value of randomness at which collapse takes place is changed. Therefore, it seems likely that our conclusions would be valid even if one included excluded volume interaction. This, however needs further investigation.

Appendix A

To prove eq 12 of the text, consider the function $Q(\vec{r},\vec{r}';N)$, defined by

$$Q(\vec{r},\vec{r}';N) = \zeta(\vec{r},\vec{r}';N) + \zeta(P\vec{r},\vec{r}';N) \qquad (A1)$$

where $P\vec{r} = (\tilde{x},-z)$. Clearly $Q(\vec{r},\vec{r}';N)$ is an even function of z. On differentiating $Q(\vec{r},\vec{r}';N)$ and evaluating it at $z = +0$, we get

$$[\partial Q(\vec{r},\vec{r}';N)/\partial z]_{z=+0} = [\partial \zeta(\vec{r},\vec{r}';N)/\partial z]_{z=+0} - $$
$$[\partial \zeta(\vec{r},\vec{r}';N)/\partial z]_{z=-0} \quad (A2)$$

From eq 8 we find

$$(\partial/\partial z)\zeta(\vec{r},\vec{r}';N)|_{z=-0}^{z=+0} = -2c_0\zeta(\vec{r},\vec{r}';N)|_{z=0} \qquad (A3)$$

From the eq A1

$$Q(\vec{r},\vec{r}';N)|_{z=0} = 2\zeta(\vec{r},\vec{r}';N)|_{z=0} \qquad (A4)$$

Combining eqs A2, A3, and A4, we get

$$[\partial Q(\vec{r},\vec{r}';N)/\partial z]_{z=+0} = -c_0 Q(\vec{r},\vec{r}';N)|_{z=0} \qquad (A5)$$

or

$$[\partial \ln Q(\vec{r},\vec{r}';N)/\partial z]_{z=+0} = -c_0 \qquad (A6)$$

Further, it is clear that for $z > 0$ $Q(\vec{r},\vec{r}';N)$ obeys the equation

$$\{\partial/\partial N - (1/6)\nabla^2\}Q(\vec{r},\vec{r}';N) = \delta(N)\,\delta(\vec{r}-\vec{r}') \qquad (A7)$$

Therefore, we conclude that $G(\vec{r},\vec{r}';N)$ and $Q(\vec{r},\vec{r}';N)$ are identical. Hence

$$G(\vec{r},\vec{r}';N) = \zeta(\vec{r},\vec{r}';N) + \zeta(P\vec{r},\vec{r}';N) \qquad (A8)$$

which is the desired result.

Appendix B

$$Z_t = \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{0}} D\vec{r}(s)\,\exp[-S_t[\vec{r}(s)]] =$$
$$N_0\int d\tilde{y}\int_{\vec{r}(0)=\vec{0}}^{\vec{r}(N)=\vec{0}}D\vec{r}(s)\,\exp\{-S_t^{\tilde{y}}[\vec{r}(s)]\} =$$
$$N_0 G_\delta(0,0;N)\int d\tilde{y}\,G_{h0}^{\tilde{y}}(\vec{0},\vec{0};N) =$$
$$N_0 G_\delta(0,0;N)\int d\tilde{y}\,G_{h0}(\tilde{y},\tilde{y};N) =$$
$$N_0 G_\delta(0,0;N)/[2\sinh(qN/6)]^2 \quad (B1)$$

As our interest is in the description of the adsorbed state, we take only the corresponding part from $G_\delta(0,0;N)$, which is equal to $\psi_b(0)^2\exp(-\epsilon_b N)$. Then

$$Z_t = N_0\psi_b(0)^2\exp(-\epsilon_b N)[2\sinh(qN/6)]^{-2} \quad (B2)$$

In the limit of large N (i.e., in the ground-state dominance approximation), one gets

$$Z_t \approx q^2 N\psi_b(0)^2\exp(-qN/3-\epsilon_b N)/(6\pi l) \quad (B3)$$

(i) $\quad (q^2/12lN)\int_0^N ds\int_0^N dt\,\langle[\tilde{x}(s)-\tilde{x}(t)]^2\rangle_T =$

$$-(q/2)(\partial/\partial q)(\ln[\prod_{\alpha=1}^n\int_{\tilde{x}_\alpha(0)=\vec{0}}^{\tilde{x}_\alpha(N)=\vec{0}}D\tilde{x}_\alpha(s_\alpha)]\exp[-S_T]) =$$

$$nq(\partial/\partial q)[\ln\sinh(qN/6)] = (nqN/6)\coth(/qN/6) \quad (B4)$$
$$\approx nqN/6 \quad (B5)$$

in the $qN/3 \gg 1$ limit.

(ii) $$\langle l(c_0 - c)/3 \int_0^N \delta(z_\alpha(s)) ds \rangle_T$$

which can evaluated similarly to be $l(c_0 - c)cN/3$.

Appendix C

Evaluation of $I_{\alpha\alpha}$ and $I_{\alpha\beta}$. We have to calculate $\sum_{\alpha,\beta=1}^{n} I_{\alpha\beta}$ where

$$I_{\alpha\beta} = \int_0^N ds \int_0^N dt \, \langle B(\tilde{x}_\alpha(s) - \tilde{x}_\beta(t)) \delta(z_\beta(t)) \, \delta(z_\alpha(s)) \rangle_T \quad (C1)$$

If $\alpha = \beta$, then we find

$$I_{\alpha\alpha} = [lcV/3]^2 \int_0^N dt_\alpha \int_0^N dt_\beta \int_{\tilde{x}_\alpha(0)=\vec{0}}^{\tilde{x}_\alpha(N)=\vec{0}} D\tilde{x}(t) \, e^{-S_t} \times$$

$$\exp[-[\tilde{x}_\alpha(t) - \tilde{x}_\beta(s)]^2/R_0^2]/2 \int_{\tilde{x}_\alpha(0)=\vec{0}}^{\tilde{x}_\alpha(N)=\vec{0}} D\tilde{x}(t) \, e^{-S_t} \quad (C2)$$

Following eq C2, we get

$$I_{\alpha\alpha} = {}^1/_2 \left[\frac{lcV}{3}\right]^2 \int_0^N dt_\alpha \int_0^N dt_\beta \int d\tilde{x}_2 \int d\tilde{x}_1 \times$$

$$\exp[-[\tilde{x}_1 - \tilde{x}_2]^2/R_0^2 \int d\tilde{y} \, G_{h0}^{\tilde{y}}(\vec{0},N|\tilde{x}_2,t_\beta) \, G_{h0}^{\tilde{y}}(\tilde{x}_2,t_\beta|\tilde{x}_1,t_\alpha) \times$$

$$G_{h0}^{\tilde{y}}(\tilde{x}_1,t_\alpha|\vec{0},0) \quad (C3)$$

We evaluate the above integral, using two approaches, viz., the ground-state dominance approximation and exact, numerical evaluation. In the ground-state dominance approximation, we get

$$I_{\alpha\alpha} \simeq (NVlc/3)^2/\{2[1 + 2l/(qR_0^2)]\} \quad (C4)$$

Analytical evaluation of the right-hand side of eq C3 using the propagator in eq 37 gives

$$I_{\alpha\alpha} = (lc/3)^2 2\bar{V}^2 \int_0^{\bar{N}} t \, dt \left[1 + \right.$$

$$(4/\bar{q}\bar{R}_0^2)\frac{\sinh(\bar{q}t/3) \sinh(\bar{q}(\bar{N} - t)/3)}{\sinh(\bar{q}\bar{N}/6)} \Bigg]^{-1} =$$

$$(\bar{c}\bar{V})^2 \frac{1}{(a^2 - b^2)^{1/2}} \ln\left[\frac{(a + b) + (a^2 - b^2)^{1/2} \tanh(\bar{q}\bar{N}/6)}{(a + b) - (a^2 - b^2)^{1/2} \tanh(\bar{q}\bar{N}/6)}\right]$$

$$(C5)$$

with $a = 1 + (2/\bar{q}\bar{R}_0^2) \coth(\bar{q}\bar{N}/3)$ and $b = -(2/\bar{q}\bar{R}_0^2) \text{cosech}(\bar{q}\bar{N}/3)$.

In the case of $I_{\alpha\beta}$, one finds

$$I_{\alpha\beta} = {}^1/_2[lcV/3]^2 \int_0^N dt_\alpha \int_0^N dt_\beta \int d\tilde{x}_2 \int d\tilde{x}_1 \times$$

$$\exp[-[\tilde{x}_1 - \tilde{x}_2]^2/R_0^2 \int d\tilde{y}_\alpha \int d\tilde{y}_\beta \, G_{h0}^{\tilde{y}_\alpha}(\vec{0},N|\tilde{x}_1,t_\alpha) \times$$

$$G_{h0}^{\tilde{y}_\alpha}(\tilde{x}_1,t_\alpha|\vec{0},0) \, G_{h0}^{\tilde{y}_\beta}(\vec{0},N|\tilde{x}_2,t_\beta) \, G_{h0}(\tilde{x}_2,t_\beta|\vec{0},0) \quad (C6)$$

The ground-state dominance approximation gives

$$I_{\alpha\beta} \simeq (NVlc/3)^2/2[1 + 4l/(qR_0^2)] \quad (C7)$$

whereas the exact evaluation of eq C6 gives

$$I_{\alpha\beta} = (lcV)^2 \int_0^1 \frac{ds}{(a_1^2 - b_1^2)^{1/2}} \times$$

$$\ln\left[\frac{(a_1 + b_1) + (a_1^2 - b_1^2)^{1/2} \tanh(\bar{q}\bar{N}/12)}{(a_1 + b_1) - (a_1^2 - b_1^2)^{1/2} \tanh(\bar{q}\bar{N}/12)}\right] \quad (C8)$$

where

$$a_1 = 1 + ((2/\bar{q}\bar{R}_0^2)/[\sinh(\bar{q}\bar{N}/6)])[2 \coth(\bar{q}\bar{N}/3) - \cosh(\bar{q}\bar{N}s/6)]$$

$$b_1 = -(2/\bar{q}\bar{R}_0^2)/[\sinh(\bar{q}\bar{N}/6)]$$

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