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Adsorption of polymers on a random surface

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We investigate the adsorption of a polymer on a planar, random surface. For this we use a generalization of de Gennes's boundary condition to a random one, and path-integral methods. For weak randomness, the chain size is reduced slightly from its value in the absence of randomness. But as one increases the randomness or chain length, the chain size becomes $\sim R$, where R is the correlation length of the potential. If the length or the randomness exceeds a certain critical value, the chain is found to collapse in the direction perpendicular to the surface, to a thickness zero, so that it becomes a two-dimensional object.

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The adsorption of polymers on surfaces has been a subject of extensive experimental and theoretical investigations. Most theoretical attempts except those of Ref. [1] have focused on planar, uniform surfaces. In the following, we introduce and analyze a model for adsorption on a planar, but random surface. The randomness may be caused by impurities on the surface or because the adsorption is on the surface of an alloy, which has a random distribution of its components on the surface. We investigate the problem using the Edwards Hamiltonian [2,3], which has been extensively used in theoretical investigations of polymer problems.

We denote the coordinates of a point as $\mathbf{r}=(\mathbf{x},z)$, where $\mathbf{x}$ stands for (x,y). The solid occupies the space $z<0$. de Gennes [4] has investigated the adsorption of polymers on a planar surface using the Schrödinger-like equation

$$\left[\frac{\partial}{\partial N}-\frac{1}{6}\nabla^2\right]G(\mathbf{r},\mathbf{r}';N)=\delta(N)\delta(\mathbf{r}-\mathbf{r}') \tag{1}$$

for the propagator $G(\mathbf{r},\mathbf{r}';N)$. The above equation is solved in the region $z>0$, with the attractive interaction with the wall being accounted for by the boundary condition

$$\left[\frac{\partial \ln}{\partial z}G(\mathbf{r},\mathbf{r}';N)\right]_{z=0}=-c_0 \ . \tag{2}$$

This prescription can easily be converted into a path-integral one, in which the paths are unconstrained and not forbidden from entering the region $z<0$, which is very convenient. $G(\mathbf{r},\mathbf{r}';N)$ is thus given by

$$G(\mathbf{r},\mathbf{r}';N)=\mathcal{G}(\mathbf{r},\mathbf{r}';N)+\mathcal{G}(\mathcal{P}\mathbf{r},\mathbf{r}';N) \ , \tag{3}$$

where $\mathcal{P}\mathbf{r}=(\mathbf{x},-z)$ and $\mathcal{G}(\mathbf{r},\mathbf{r}';N)$ is defined by

$$\mathcal{G}(\mathbf{r},\mathbf{r}';N)=\int_{\mathbf{r}(0)=\mathbf{r}'}^{\mathbf{r}(N)=\mathbf{r}}D\mathbf{r}(s)\exp\{-S_\delta[\mathbf{r}(s)]\}/\mathcal{N} \ , \tag{4}$$

where

$$S_\delta[\mathbf{r}(s)]=S_0[\mathbf{r}(s)]-(lc_0/3)\int_0^N\delta(z(s))ds \ , \tag{5}$$

with

$$S_0[\mathbf{r}(s)]=\frac{3}{2l}\int_0^N ds\left[\frac{d\mathbf{r}(s)}{ds}\right]^2 \tag{6}$$

and

$$\mathcal{N}=\int d\mathbf{r}\int_{\mathbf{r}(0)=\mathbf{r}'}^{\mathbf{r}(N)=\mathbf{r}}D\mathbf{r}(s)\exp\{-S_\delta[\mathbf{r}(s)]\} \ . \tag{7}$$

The paths in Eq. (7) may enter the region $z<0$ too. We model the adsorption on a planar, random surface by modifying the boundary condition of Eq. (2) to

$$\left[\frac{\partial \ln}{\partial z}G(\mathbf{r},\mathbf{r}';N)\right]_{z=0}=-[c_0+v(\mathbf{x})] \ , \tag{8}$$

where $v(\mathbf{x})$ is a random function of $\mathbf{x}$. We take it to be Gaussian with mean zero and correlation function $\langle v(\mathbf{x})v(\mathbf{x}')\rangle=B(\mathbf{x}-\mathbf{x}')$, where $\langle\ \rangle$ denotes averaging with respect to the random function. In the following, we consider randomness with a correlation length R, and take $B(\mathbf{x})=V^2\exp[-\mathbf{x}^2/R^2]$. $G(\mathbf{r},\mathbf{r}';N)$ is now a functional of $v(\mathbf{x})$ and is still given by Eq. (3) with

$$\mathcal{G}(\mathbf{r},\mathbf{r}';N)=\int_{\mathbf{r}(0)=\mathbf{r}'}D\mathbf{r}(s)\exp\{-S_{\rm ran}[\mathbf{r}(s)]\}\times\delta(\mathbf{r}(N)-\mathbf{r})/\mathcal{N}_{\rm ran} \ . \tag{9}$$

Here

$$\mathcal{N}_{\rm ran}=\int d\mathbf{r}\int_{\mathbf{r}(0)=\mathbf{r}'}D\mathbf{r}(s)\exp\{-S_{\rm ran}[\mathbf{r}(s)]\}\delta(\mathbf{r}(N)-\mathbf{r}) \tag{10}$$

and

$$S_{\rm ran}[\mathbf{r}(s)]=S_\delta[\mathbf{r}(s)]-\frac{l}{3}\int_0^N v(\mathbf{x}(s))\delta(z(s))ds \ . \tag{11}$$

Formally, introducing n replicas, labeled with $\alpha=1,2,\ldots,n$, one can write

$$\mathcal{G}(\mathbf{r},\mathbf{r}';N)=\lim_{n\to 0}\prod_{\alpha=1}^{n}\int_{\mathbf{r}_\alpha(0)=\mathbf{r}'}D\mathbf{r}_\alpha(s_\alpha)\exp\{-S_{\rm ran}[\mathbf{r}_\alpha(s_\alpha)]\}\delta(\mathbf{r}_1(N)-\mathbf{r})\ . \tag{12}$$

On performing the average over the random function $v(\mathbf{x})$, we get

$$\langle\mathcal{G}(\mathbf{r},\mathbf{r}';N)\rangle=\lim_{n\to 0}\left[\prod_{\alpha=1}^{n}\int_{\mathbf{r}_\alpha(0)=\mathbf{r}'}D\mathbf{r}_\alpha(s_\alpha)\right]\times\exp[-S]\delta(\mathbf{r}_1(N)-\mathbf{r})\ , \tag{13}$$

where

$$S=\sum_\alpha S_\delta[\mathbf{r}_\alpha(s_\alpha)]-S_1 \tag{14}$$

with

$$S_1=\frac{l}{2}\left[\frac{1}{3}\right]^2\sum_{\alpha,\beta=1}^{n}\int_0^N ds\int_0^N dt\,B(\mathbf{x}_\alpha(s)-\mathbf{x}_\beta(t))\times\delta(z_\alpha(t))\delta(z_\beta(s))\ . \tag{15}$$

Our interest is only in adsorbed molecules, for which we would like to calculate $\langle[\mathbf{r}(N)-\mathbf{r}(0)]^2\rangle$. The integral in Eq. (13) cannot be evaluated analytically. So we adopt the variational method, with the trial action

$$S_T=\sum_{\alpha=1}^{n}S_t[\mathbf{r}_\alpha(s_\alpha)]\ , \tag{16}$$

where

$$S_t[\mathbf{r}(s)]=S_0[\mathbf{r}(s)]-(lc/3)\int_0^N\delta(z(s))ds+(q^2/12lN)\int_0^N ds\int_0^N dt\,[\mathbf{x}(s)-\mathbf{x}(t)]^2\ . \tag{17}$$

c and q are trial parameters. Note that the action in Eq. (17) has a δ-function attractive part as well as a harmonic-oscillator-like nonlocal part [last term in Eq. (17)]. We prefer to use this nonlocal action rather than the one used in Ref. [5], as this action is unchanged by translations parallel to the surface, whereas the one in Ref. [5] is not. With this trial action, all path integrals that are needed for our purpose can be evaluated. For example, consider the propagator for the trial action, defined by

$$G_t(\mathbf{r},\mathbf{r}';N)=\frac{I(\mathbf{r},\mathbf{r}';N)}{\int d\mathbf{r}I(\mathbf{r},\mathbf{r}';N)}\ , \tag{18}$$

with

$$I(\mathbf{r},\mathbf{r}';N)=\int_{\mathbf{r}(0)=\mathbf{r}'}D\mathbf{r}(s)\exp\{-S_t[\mathbf{r}(s)]\}\delta(\mathbf{r}(N)-\mathbf{r})\ . \tag{19}$$

Following Ref. [6] it is possible to write the above as

$$G_t(\mathbf{r},\mathbf{r}';N)=\frac{\int d\mathbf{y}\int_{\mathbf{r}(0)=\mathbf{r}'}^{\mathbf{r}(N)=\mathbf{r}}D\mathbf{r}(s)\exp[-S_t^{\mathbf{y}}]}{\int d\mathbf{r}\int d\mathbf{y}\int_{\mathbf{r}(0)=\mathbf{r}'}^{\mathbf{r}(N)=\mathbf{r}}D\mathbf{r}(s)\exp[-S_t^{\mathbf{y}}]}\ , \tag{20}$$

where

$$S_t^{\mathbf{y}}[\mathbf{r}(s)]=S_0[\mathbf{r}(s)]-(lc/3)\int_0^N\delta(z(s))ds+(q^2/6l)\int_0^N ds\,[\mathbf{x}(s)-\mathbf{y}]^2\ . \tag{21}$$

In the above, $\mathbf{y}=(y_1,y_2)$ is a two-dimensional vector. The above identity is quite interesting in that the nonlocal harmonic-oscillator-like part has been replaced by a quadratic interaction with the point $\mathbf{y}$, with subsequent integration over $\mathbf{y}$. As the $\mathbf{x}$ and z are not coupled in Eqs. (20) and (21), one gets

$$G_t(\mathbf{r},\mathbf{r}';N)=\frac{I_1(\mathbf{r},\mathbf{r}';N)}{\int d\mathbf{r}\,I_1(\mathbf{r},\mathbf{r}';N)}\ , \tag{22}$$

with

$$I_1(\mathbf{r},\mathbf{r}';N)=G_\delta(z,z';N)\int d\mathbf{y}\,G_{\rm ho}^{\mathbf{y}}(\mathbf{x},\mathbf{x}';N)\ . \tag{23}$$

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

$$\left[\frac{\partial}{\partial N}-\frac{l}{6}\frac{\partial^2}{\partial z^2}-c\delta(z)\right]G_\delta(z,z';N)=\delta(N)\delta(z-z')\ . \tag{24}$$

$G_{\rm ho}^{\mathbf{y}}(\mathbf{x},\mathbf{x}';N)$ corresponds to Brownian motion in a plane, with parabolic sink, having origin at $\mathbf{y}$ and satisfies

$$\left[\frac{\partial}{\partial N}-\frac{l}{6}\nabla_{\mathbf{x}}^2-\frac{q^2}{6}(\mathbf{x}-\mathbf{y})^2\right]G_{\rm ho}^{\mathbf{y}}(\mathbf{x},\mathbf{x}';N)=\delta(N)\delta(\mathbf{x}-\mathbf{x}')\ . \tag{25}$$

"ho" stands for harmonic oscillator. Explicit expressions for both $G_\delta(z,z';N)$ and $G_{\rm ho}^{\mathbf{y}}(\mathbf{x},\mathbf{x}';N)$ are available. Hence $G_t(\mathbf{r},\mathbf{r}';N)$ is known. If $c>0$, then the operator $-(l/6)\partial^2/\partial z^2-c\delta(z)$ 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 state of the polymer. As the paths are not restricted to the region with $z>0$, the normalization that we use is $\int_{-\infty}^{\infty}dz\,\psi_b(z)^2=1$. In the limit where N becomes large, the two propagators are dominated by the lowest possible eigenfunctions, and hence one has

$$G_\delta(z,z';N)\approx c\exp\{-c(|z|+|z'|)-\epsilon_b N\} \tag{26}$$

and

$$G_{\rm ho}^{\mathbf{y}}(\mathbf{x},\mathbf{x}';N)\approx\exp[-q\{(\mathbf{x}-\mathbf{y})^2+(\mathbf{x}'-\mathbf{y})^2\}/(2l)-qN/3]q/(\pi l)\ . \tag{27}$$

Remembering that our parameters c and q have to be determined so as to best suit the description of adsorbed polymers, we make use of the Feynman variational procedure (see Refs. [5] and [7]), for their determination. Thus, we expect the integral

$$I(n)=\left[\prod_{\alpha=1}^{n}\int_{\mathbf{r}_\alpha(0)=0}^{\mathbf{r}_\alpha(N)=0}D\mathbf{r}_\alpha(s_\alpha)\right]\exp[-S] \tag{28}$$

to behave like $\exp[-nE(N)]$ for $n\to 0$ and large N. We

estimate $E_0(N)$ 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 $\langle [\mathbf{r}(N)-\mathbf{r}(0)]^2 \rangle$. Thus

$$I(n)=\left[\prod_{\alpha=1}^{n}\int_{\mathbf{r}_\alpha(0)=0}^{\mathbf{r}_\alpha(N)=0} D\mathbf{r}_\alpha(s_\alpha)\right]\exp[-S_T]$$
$$\times\langle \exp-(S-S_T)\rangle_T$$
$$\geq Z_t^n \exp\langle -(S-S_T)\rangle_T \ , \qquad (29)$$

where $\langle\ \rangle_T$ denotes averaging with respect to S_T and

$$Z_t=\int_{\mathbf{r}(0)=0}^{\mathbf{r}(N)=0} D\mathbf{r}(s)\exp\{-S_t[\mathbf{r}(s)]\}$$
$$=N_0\int d\mathbf{y}\int_{\mathbf{r}(0)=0}^{\mathbf{r}(N)=0} D\mathbf{r}(s)\exp\{-S_t^{\mathbf{y}}[\mathbf{r}(s)]\}$$
$$=N_0 G_\delta(0,0;N)\int d\mathbf{y}\, G_{\mathrm{ho}}^{\mathbf{y}}(\mathbf{0},\mathbf{0};N)$$
$$=N_0 G_\delta(0,0;N)/[2\sinh(qN/6)]^2 \ , \qquad (30)$$

with $N_0=q^2N/(6\pi l)$. 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 $\psi_b(0)^2\exp[-\epsilon_b N]$. In the limit of large N, one gets $Z_t \approx q^2 N\psi_b(0)^2\exp(-qN/3-\epsilon_b N)/(6\pi l)$. The integrals that occur in $\langle S-S_T\rangle$ are

(i) $\sum_{\alpha=1}^{n}(q^2/12lN)\int_0^N ds\int_0^N dt\langle[\mathbf{x}_\alpha(s)-\mathbf{x}_\alpha(t)]^2\rangle_T$

$$=-(q/2)\frac{\partial}{\partial q}\left[\ln\left[\prod_{\alpha=1}^{n}\int_{\mathbf{r}_\alpha(0)=0}^{\mathbf{r}_\alpha(N)=0} D\mathbf{r}_\alpha(s_\alpha)\right]\exp[-S_T]\right]$$
$$=nq\frac{\partial}{\partial q}[\ln\sinh(qN/6)]=(nqN/6)\coth(qN/6)\approx nqN/6 \quad \text{in the } qN/3\gg 1 \text{ limit} \ . \qquad (31)$$

(ii) $\sum_{\alpha=1}^{n}\langle l(c-c_0)\int_0^N\delta(z_\alpha(s))ds/3\rangle_T$, which can be evaluated to be $nl(c-c_0)cN/3$. (iii) $\sum_{\alpha,\beta=1}^{n} I_{\alpha\beta}$, where

$$I_{\alpha\beta}=\frac{1}{2}\left[\frac{l}{3}\right]^2\int_0^N ds\int_0^N dt\langle B[\mathbf{x}_\alpha(s)-\mathbf{x}_\beta(t)]$$
$$\times\delta(z_\beta(t))\delta(z_\alpha(s))\rangle_T \ . \qquad (32)$$

$I_{\alpha\alpha}$ can be evaluated analytically. $I_{\alpha\beta}$ with $\alpha\neq\beta$ can be found numerically. As the results are tedious to analyze, we use the ground-state dominance approximation [5] to get the following: $I_{\alpha\alpha}\approx(NVlc/3)^2/\{2[1+2l/(qR^2)]\}$ and $I_{\alpha\beta}\approx(NVlc/3)^2/\{2[1+4l/(qR^2)]\}$. Combining the above results, and introducing the dimensionless variables $\bar{N}=N/l$, $\bar{c}=cl$, $\bar{q}=ql$, $\bar{R}=R/l$, $\bar{c}_0=c_0 l$, $\bar{V}=Vl$, we get

$$E_0(N)/\bar{N}=[\bar{c}^2-2\bar{c}\,\bar{c}_0+u/\bar{R}^2-\bar{c}^2 f(u)]/6 \ , \qquad (33)$$

where $f(u)=pu/[(2+u)(4+u)]$, $p=2\bar{N}\bar{V}^2/3$, and $u=\bar{q}\bar{R}^2$. In Eq. (33), $\bar{c}^2$ 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, $u/\bar{R}^2$ the price for localizing the chain to dimensions of q^{-1} in directions parallel to the surface, and $-\bar{c}^2 f(u)$, the effect of the randomness, which results in a net attraction between the chains, as indicated by the negative sign. Note that this term has $-\bar{c}^2$ because of the lowering of energy caused by adsorption. 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}. From the trial action, we find $\langle[\mathbf{x}(N)-\mathbf{x}(0)]^2\rangle=2l^2\bar{R}^2\tanh[u\bar{N}/(6\bar{R}^2)]/u$, using which the size of the chain parallel to the surface can be estimated. We now find the best values of u and $\bar{c}$, which make $E_0(N)$ a minimum.

Case I: $p<p^0$. Here, $p^0=[8+\sqrt{32}]$. Finding the value of c such that $E_0(N)$ is a minimum gives $\bar{c}=\bar{c}_0/[1-f(u)]$. Note that if $\bar{c}$ is negative, there is no bound (adsorbed) state, which violates our basic assumption in deriving Eq. (25). Therefore only $\bar{c}>0$ is acceptable to us, and this is satisfied if $p<p^0$. Using this value of $\bar{c}$, we get

$$6E_0(N)\bar{R}^2/\bar{N}=-(\bar{c}_0\bar{R})^2+u$$
$$-p_1 u/[(2+u)(4+u)-pu] \ , \qquad (34)$$

where $p_1=\bar{R}^2\bar{c}_0^2 p$. One can now analyze (34) to find the following results: If $p_1<p_1^0$, where $p_1^0=8$, then $E_0(N)$ has its minimum at $u=0$. The size of the chain in the parallel direction is $\langle[\mathbf{x}(N)-\mathbf{x}(0)]^2\rangle=l^2\bar{N}/3$, indicating that the chain is unaffected by the randomness. Strictly speaking, this is an artifact of our ground-state dominance approximation, which breaks down if $u=0$ (i.e., when $q=0$). A more rigorous analysis shows that the chain size is decreased in both parallel and perpendicular directions by the randomness. If $p_1>p_1^0$, then the minimum occurs at $u>0$. As $p_1\to\infty$, the minimum tends to be at $u=\sqrt{8}$, so that $\langle[\mathbf{x}(N)-\mathbf{x}(0)]^2\rangle=2l^2\bar{R}^2\tanh[\sqrt{8}\bar{N}/(6\bar{R}^2)]/(\sqrt{8})\to 2l^2\bar{R}^2/(\sqrt{8})$, indicating that the chain occupies only regions of size $\approx R$.

Case II: $p>p^0$. In this case, $f(u)$ is greater than 1 for a range of values of u (or equivalently q). $E_0(N)$ has its minimum value for $c=\infty$, thus indicating that the adsorbed state is collapsed in the direction perpendicular to the surface. The chain is now two dimensional. To get its size, we make use of Eq. (33). If $\bar{c}\to\infty$ then the important term in this equation is $\bar{c}^2[1-f(u)]/6$ and this has its least value when $u=\sqrt{8}$.

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