Adsorption assisted translocation of a chain molecule through a pore in a spherical vesicle

K. Kiran Kumar* and K.L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bangalore 560012
India
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We analyze the free energy for translocation of a polymer from the outside of a spherical vesicle to the inside. The process is assumed to be driven by the adsorption of the polymer on the inner surface of the vesicle. We argue that in the case where the polymer is adsorbed on the outer surface too, the entropic barrier for translocation is absent. We analyze the adsorption energy and find the free energy profile for the process. We argue that the motion corresponds to a polymer crossing a region with a change in free energy per segment. Based upon our earlier analysis of the behaviour of kinks in such a problem, we conclude that the translocation can occur with a crossing time $t_{\text{cross}} \sim N$.

I. INTRODUCTION

Translocation of a long chain molecule through a pore (see figure 1A) has been a problem of current interest [1], [2]. Park and Sung [1] have studied the problem of release of a polymer through a small pore in a spherical vesicle. Their primary results concern the entropy effects in driving the polymer from the inside to the outside of the spherical vesicle. They calculate the time taken by a polymer molecule to translocate through the pore. They have considered both the inner and the outer surfaces of the vesicle to be hard walls, which repel the units of the long chain molecule. They argue (a) that the membrane curvature drives the polymer out of a spherical vesicle (b) capture of a polymer of $N$ segments into a small bud takes a very long time proportional to $\exp(N)$, which can be reduced to $N^3$ or even to $N^2$ by free energy differences between the inside and the outside. In this paper, we consider the case where there may be adsorption on both the surfaces. We construct a free energy profile for the translocation process. We show that in the case, the entropic barrier for penetration into the pore is absent. Following the reference [3], we suggest that translocation can occur by kink motion and this is driven by the free energy difference due to the different adsorption strengths. This can lead to a translocation time $t_{\text{cross}} \sim N$.

We make use of the approach of de Gennes [4] to treat the adsorption of the chain molecule on the surfaces [5]. We go beyond the results of Park and Sung [1] and find the exact partition function for a chain restricted to the outer of a sphere and having an attractive interaction with the surface of the sphere. For a chain molecule confined to the inner region of the sphere and interacting with the surface, we give the exact result for the Laplace transform of the partition function. We analyze the condition for the existence of an adsorbed state and find that they are different for the two cases. Partition function is found in the limit of a long chain and this is used to calculate the free energy of the adsorbed polymer. From this, we construct the free energy profile for the translocation process.

II. GREEN’S FUNCTIONS FOR ADSORPTION PROBLEMS

We wish to evaluate the partition function for a chain of $n$ segments confined to the outer region or inner region of a sphere. For this, we consider the Green’s function $G(r,r_0;n)$, obeying the equation $\left(\frac{\partial}{\partial n} - \frac{k^2}{6} \nabla^2 + V(r)\right)G(r,r_0;n) = \delta(n)\delta(r-r_0)$ (see [1] for more details). $V(r)$ is the potential of interaction arising from the sphere. The partition function for the polymer may be calculated from the angle averaged function $Z(r,r_0;n) = \int_0^\pi d\theta \int_0^{2\pi} d\phi \sin(\theta)G(r,r_0;n)$. This averaged Green’s function obeys the simpler equation [6].

*permanent address: Department of Chemistry Indian Institute of Technology Kharagpur India
\[
\left( \frac{\partial}{\partial n} - \frac{a^2}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + V(r) \right) Z(r, r_0; n) = \frac{1}{r^2} \delta(n) \delta(r - r') \tag{1}
\]

where \( a = b/\sqrt{6} \). The conditions on \( Z(r, r_0; n) \) are that \( Z(r, r_0; n) \to 0 \) as \( r, r_0 \to \infty \). In the case \( V(r) = 0 \), we can solve this equation easily to obtain

\[
Z_0(r, r'; n) = \frac{1}{rr_0 \sqrt{\pi n}} \exp\left\{ -\frac{(r^2 + r_0^2)}{4a^2 n} \right\} \sinh\left( \frac{rr_0}{2a^2 n} \right) \tag{2}
\]

The presence of a spherical surface at \( r = R \) with a short range attractive (or repulsive) potential can be accounted for by imposing the de Gennes’ boundary condition \( \left( \frac{d \ln Z(r, r_0; n)}{dr} \right)_{r=R} = c_0 \). If \( c_0 \to \infty \), the surface is a hard wall. \( c_0 = 0 \) represents a neutral surface, while \( c_0 < 0 \) models an attractive surface. We now use this to solve the problem of adsorption on the outside of a sphere. It is easier to work with the Laplace transform of the Green’s function \( \bar{Z}(r, r'; s) = \int_0^\infty dZ(r, r'; n)e^{-sn} \). It obeys the differential equation

\[
\left( s - \frac{a^2}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) \bar{Z}(r, r_0; s) = \frac{1}{r^2} \delta(r - r_0) \tag{3}
\]

and the boundary condition becomes

\[
\left( \frac{d \ln \bar{Z}(r, r_0; s)}{dr} \right)_{r=R} = c_0 \tag{4}
\]

A. Adsorption on the outer surface of a sphere

We now solve the equation (3) in the region outside the sphere \( (r > R) \) subject to the de Gennes’ boundary condition to obtain \( Z_\geq(r, r_0; s) \). We get

\[
Z_\geq(r, r_0; n) = \frac{1}{2a \sqrt{\pi n}} \frac{c}{rr_0} e^{c^2 n + c(r-2R+r_0)} E_{\text{rf}c}(ac \sqrt{n} + \frac{r-2R+r_0}{2a \sqrt{n}}) \tag{5}
\]

where \( c = (c_0 + \frac{1}{R}) \), and \( E_{\text{rf}c} \) is the complementary error function. This is similar to the expression for the case of adsorption on a planar surface (4). As the wall becomes repulsive \( (c \to \infty) \), the above reduces to the solution for absorbing barrier condition:

\[
Z_\geq(r, r_0; n) = \exp\left\{ -\frac{(r-r_0)^2}{4a^2 n} \right\} - \exp\left\{ \frac{(r+r_0-2R)^2}{4a^2 n} \right\} \frac{2ar_0 \sqrt{\pi n}}{2a \sqrt{n}} \tag{6}
\]

Note that in the limit \( R \to 0 \) the parameter \( c \to \infty \) and the result is the free space solution of equation (3).

B. Partition function for a polymer with one end on the surface

We find the partition function for the polymer with the end \( r_0 \) fixed at the surface of the sphere \( (r_0 = R) \) and the other end free. This is found by integrating over all the values of \( r \). That is, \( Q_{\geq}(n) = \int_R^\infty dr Z_\geq(r, R; n)r^2 \). The result is

\[
Q_{\geq}(n) = \frac{1}{c R} \left( 1 + e^{a^2 c^2 n} (-1 + c R) E_{\text{rf}c}(ac \sqrt{n}) \right) \tag{7}
\]
We now consider the limit where \( n \to \infty \). If \( c < 0 \), then we can approximate the above as \( Q_<(n) \sim \frac{d}{dn} \left( R c - 1 \right) e^{a n} c^2 \). In this limit, the free energy of a polymer, having \( n \) units, with one end at \( R \) is
\[
F(n) = -k_B T \ln Q_<(n) \simeq -k_B T a^2 n c^2.
\]
This gives a free energy per unit equal to \(-k_B T a^2 c^2\) for the chain on the outer surface of the sphere. This free energy primarily comes from the bound (adsorbed) state on the surface of the sphere. We can also ask: what is the condition for the existence of the bound state? Obviously, it would be there, if \( c_0 < 0 \). In contrast to the situation on a planar surface where the condition is \( c_0 < -1/R \), in this case, the attractive interaction has to below a finite critical value - that is \( c_0 < -1/R \), to have a bound state.

**C. Adsorption on the inner surface of the sphere**

For the case where the polymer is inside the vesicle the boundary condition we impose is
\[
\left( \frac{d\ln Z_r(r_0,s)}{dr} \right)_{r=R} = -d_0.
\]
Note that we have put a negative sign in front of \( d_0 \) (compare the equation \( [3] \) ) as increasing the value of \( r \) means one is moving towards the surface). One can explicitly evaluate the Laplace transform of the propagator. On solving the equation \( [3] \) we find
\[
Z_<(r, r_0; s) = \frac{\sinh \left( \frac{\sqrt{s}}{a} r \right)}{a r r_0 \sqrt{s}} \left( \frac{R \sqrt{s} \cosh \left( \frac{R-r}{a} \right)}{R \sqrt{s} \cosh \left( \frac{R-r}{a} \right)} - a \sinh \left( \frac{R-r}{a} \right) + a R \sinh \left( \frac{R-r}{a} \right) d_0 \right) \right)
\]
if \( r > r_0 \) and
\[
Z_<(r, r_0; s) = \frac{\sinh \left( \frac{\sqrt{s}}{a} r \right)}{a r r_0 \sqrt{s}} \left( \frac{R \sqrt{s} \cosh \left( \frac{R-r}{a} \right)}{R \sqrt{s} \cosh \left( \frac{R-r}{a} \right)} + a \sinh \left( \frac{R-r}{a} \right) \right) \right) \right)
\]
if \( r < r_0 \).

**D. Partition function for the polymer with one end on the inner surface**

We find the partition function for the polymer with the one end fixed at the inner surface of the sphere and the other end free. This is done by putting \( r_0 = R \) and integrating over all the values of \( r \) inside the sphere. We get
\[
\bar{Q}_<(s) = \int_0^R r^2 dr Z_<(r, R; s)
\]
\[
= \frac{\sqrt{s} - \tanh \left( \frac{R \sqrt{s}}{a} \right) a / R}{s \left( \sqrt{s} + a \tanh \left( R \sqrt{s} / a \right) \right)}
\]
where \( d = d_0 - 1/R \). We can evaluate the partition function by Bromwich integration: \( Q_<(n) = \int_{\gamma-i \infty}^{\gamma+i \infty} ds e^{sn} \bar{Q}(s)/(2\pi i) \), where \( \gamma \) is taken such that it is to the right of all the poles of \( \bar{Q}_<(s) \). To find the poles of \( \bar{Q}(s) \), we solve the transcendental equation \( \tanh(x) = -x/(Rd) \), where \( x = R \sqrt{s} / a \). We consider the two different possibilities:

1. \( d_0 \) is negative. Then \( Rd < -1 \). Then one pole exists for real, positive value of \( s \). This value of \( s \) is given by \( s = (ax_r/R)^2 \), where \( x_r \) obeys \( \tanh(x_r) = -x_r/(dR) \). For this case, for large values of \( n \), the major contribution to \( Q_<(n) \) comes from this pole and hence \( Q_<(n) \sim e^{(ax_r/R)^2}n \) and the free energy of the adsorbed chain is \(-k_B T (ax_r/R)^2 n \). The free energy per unit length of the adsorbed chain is \(-k_B T (ax_r/R)^2 \). In contrast to the outer surface, there is no critical value for the logarithmic derivative, for an adsorbed state to exist. It would exist as long as the surface-segment interaction is attractive.
2. \(d_0\) is positive. In this case, all the poles have \(s < 0\) and there is no adsorbed state. There are several states inside the spherical vessel, and the Bromwich integration leads to an infinite sum for the partition function. This type of problem has already been considered in [1] and we shall not discuss this case further.

III. FREE ENERGY FOR THE TRANSLOCATION PROCESS

Let us now consider the translocation of the chain molecule. If the molecule is confined to a spherical vesicle, with the outer and inner walls of the vesicle having no affinity to the units of the chain molecule, then the free energy of the molecule inside would be greater than on the outside. Consequently, if there is a pore on the wall of the vesicle, the molecule would move from the inside to the outside. But there are examples where the molecule does the reverse [2] [8]. This would either require either a motor driving the chain in, or a situation where the chain has a lower free energy inside the vesicle. We consider the latter situation, and we assume that the polymer can adsorb on inner walls of the vesicle. (It is not necessary that the adsorption should be on the walls, it can be anywhere inside the vesicle). The process that we consider is given in the figure 1A. We assume that the strength of adsorption on the inner wall is greater, and this drives the translocation process. The translocating chain may be thought of as divided in to three portions - first is the portion adsorbed on the outside, second, the portion on the inside, and the third is the portion inside the pore. We already have expressions for the free energy per segment of the chain molecule when it is inside/outside. The portion that is inside the pore, is not adsorbed anywhere and consequently, the free energy per segment is higher. Hence, the free energy per segment for a translocating chain would have the appearance of figure 2. An alternate scenario would be to have a pore which has affinity towards the molecule, as a result of which the free energy per segment follows the dotted line in the figure 2, for segments inside the chain. Irrespective of which is the profile, if one now uses a one dimensional Rouse model to describe the process [3], then one has the following picture: the portion inside the pore is to be thought of as a kink on the chain, and it can move on the chain. In the case where there is a free energy lowering on going to the inner side, the kink will move in the opposite direction with a finite velocity (for an expression for this velocity, see [3]). Consequently, the polymer will move in to the inner side, with a constant rate. This means that the crossing time \(t_{\text{cross}} \sim N\), in contrast to \(t_{\text{cross}} \sim N^2\) or \(t_{\text{cross}} \sim N^3\), found in reference [1]. It is of interest to consider the case where the polymer is not adsorbed on the outer surface of the sphere, as in figure 1B. In this case, having one end of the polymer inside the pore would be entropically unfavorable and would lead to a barrier, purely from this (see for example, the figure 2 of reference [1]). This type of barrier is absent in our case. Thus, weak adsorption on the outer surface eliminates the entropic barrier and thus facilitates translocation in to the vesicle.

One can also consider the case of translocation from a vesicle of radius \(R_1\) to another of radius \(R_2\). Analyzing this case, Park and Sung [1] conclude that spontaneous capture in to a small bud can only rarely occur as the chain is losing entropy in going in to a small bud. However, adsorption on the surface of the bud, can drive the process. Park and Sung suggest that this will lead to at the most \(t_{\text{cross}} \sim N^2\). Motion of the kink can act as the mechanism of transfer and this can lead to capture times proportional to \(N\).

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A. Figure Captions

1. Figure 1A: Case where there is adsorption on the inside as well as outside. The translocation from the outside to the inside. The portion of the chain within the pore is indicated by enclosing it within a circle. Figure 1B: Case where there is no adsorption on the outside.

   Figure 2: The Free energy per segment as a function of segment position.
\(-k_B T a^2 c^2\)

A

Outside

\(-k_B T (a x_f / R)^2\)

In the pore

B

Inside