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Adsorption of a Ring Polymer onto a Surface

Edmund A. Di Marzio

National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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ABSTRACT: The problem of a semiflexible polymer ring consisting of N monomers and constrained to walk among M parallel layers is solved in the lattice model approximation for various lattices. The monomer units of the ring can have arbitrary interaction energies with the surface $\Delta\epsilon_i$ for layer i, and additionally, it can have an internal stiffness energy which is a function of the angle between contiguous bonds.

Introduction

The adsorption of polymer rings onto a surface has been studied by several groups both experimentally[1,2] and theoretically.[3,4] Besides being an interesting problem in its own right, one wishes to compare ring adsorption to adsorption of a linear chain. If one species adsorbs preferentially (displaces the other) when a blend of rings and linear polymers are placed above a surface, then adsorption may well provide a chromatographic or even a preparative technique for separating rings from linear chains of the same molecular weight. A second application is to predict the glass transition temperature of bulk polymer consisting of rings. The entropy theory of glass formation requires us to know the partition function for an isolated ring[5,6] as a prerequisite to calculation of the entropy equation of state. An important aspect of this calculation is to properly take into account the stiffness energy of the ring (see the Theory section). A third related application is to determine the equations of state of ring–linear polymer systems. This paper formulates and solves the problem of an isolated ring polymer between two parallel plates. We do this by modifying the linear polymer between two plates problem solved previously.[7]

Theory

For linear polymers walking on a lattice of coordination number z it has been shown that the partition function Q from which the thermodynamics can be derived is given by[7]

$$Q(M,N+1) = \mathbf{U}^{\mathrm{T}}\mathbf{W}^{N}\mathbf{P}(0) \tag{1}$$

where M is the separation between the two outside layers. $N+1$ is the number of monomer units, $\mathbf{U}^{\mathrm{T}}$ is the unit row vector (1, 1, ..., 1), $\mathbf{P}(0)$ is the column vector ($e^{\theta 1}$, 1, ..., 1, $e^{\theta M}$), and the tridiagonal matrix $\mathbf{W}$ is

$$\mathbf{W} = \begin{bmatrix} z(1-a)e^{\theta 1} & zae^{\theta 1}/2 & & & & & \\ za/2 & z(1-a) & za/2 & & & & \\ & za/2 & z(1-a) & za/2 & & & \\ & & \cdots & \cdots & \cdots & & \\ & & \cdots & \cdots & \cdots & & \\ & & & za/2 & z(1-a) & za/2 & \\ & & & & & zae^{\theta M} & z(1-a)e^{\theta M} \end{bmatrix} \tag{2}$$

Here a is the fraction of bonds that lie perpendicular to the surface, half of them stepping up and half stepping down and $1-a$ is the fraction stepping parallel to the surface. θ_1 which is $\Delta\epsilon_1/kT$ is the dimensionless energy of interaction of a monomer with surface 1. One can either view the surface at layer zero and have $\Delta\epsilon_1$ be the energy of the bond between the surface at zero and the monomer lying in layer 1 or, alternatively, view the surface and the monomer to be both in layer 1. The bonds connecting monomers that lie on the surface lie in layer 1.

The reader can verify that every possible linear sequence of the symbols, up, down, and parallel, appears once and only once in the sum given by expression 1 and is weighted with the proper Boltzmann factor.

The column vector given above is appropriate when the starting point for the first monomer is allowed to be at any level with the appropriate Boltzmann factor. However if we force the starting monomer to be at level k then $\mathbf{P}(0)$ would be replaced by $\mathbf{P}_k(0)$ which has zeros everywhere except for a 1 at level k. If $k = 1$ we use $\exp(\theta_1)$ and if $k = M$ we use $\exp(\theta_M)$. Similarly, if we wish the terminal monomer to lie in level j then we replace $\mathbf{U}^{\mathrm{T}}$ by $\mathbf{U}_j^{\mathrm{T}}$ which has 1 in the jth place and zeros elsewhere. We use 1's rather than Boltzmann factors in the first and Mth places because the matrix has provided the proper weighting.

The above expressions are valid for a chain whose monomers are distinguishable from one another, by being colored differently, for example, or by being labeled from 1 to $N+1$. However if the monomers are indistinguishable, the above formulas overcount by almost a factor of 2. A particular shape that walks from level k to j is counted as originating from layer k, but it is also counted in the matrix multiplication as originating from layer j and ending in layer k. This explains the factor of 2: however it is not quite a factor of 2 because certain shapes are counted only once. These are among the shapes that start and end at level k. A shape is characterized by a particular sequence of up, down, forward, backward and left, right (simple cubic lattice). However, if we start from the other end, this same shape is also characterized by the sequence in which up and down are interchanged, forward and backward are interchanged, and left and right are interchanged. Thus the matrix overcounts this shape by a factor of 2 since both sequences (corresponding to only one configuration) appear in the matrix multiplication. However if the two sequences thus generated are identical, the shape is counted only once by the matrix multiplication. Thus the partition function for a chain composed of indistinguishable monomers is almost a factor of 2 less than that given by eq 1. This is an unimportant effect for large N since the number of chain configurations is for the sc lattice of the order of $2^{(d-1)N}$ (d = dimension); but for small N it may matter.

Theory, One Dimension

For one dimension the ring problem is solved for a chain of distinguishable monomers by allowing the last monomer (labeled $N+1$) to end at the same level as the first monomer (labeled 1). In one dimension the beginning and ending monomers superimpose, but in $d \neq 1$, dimensions being at the same level does not mean being at the same place since the remaining $d-1$ coordinates of the two monomers may differ. For one dimension then eq 1 may be modified to give for rings

$$Q_D = \sum_{k=1}^{M} \mathbf{U}_k{}^{T}\mathbf{W}^{N}\mathbf{P}_k(0) \text{ (one dimension)} \tag{3}$$

where now the components of $\mathbf{P}_k(0)$ are

$$(\mathbf{P}_k(0))_{jk} = \delta_{jk},\ k \neq 1, M;\ (\mathbf{P}_1(0))_{j1} = \delta_{j1}e^{\theta 1},\ (\mathbf{P}_M(0))_{jM} = \delta_{jM}e^{\theta M} \tag{4}$$

and

$$(\mathbf{U}_k{}^{T})_j = \delta_{kj} \tag{4A}$$

Equation 3 is for a chain that can be anywhere within the plates. For a chain whose first segment begins at the kth level we have just the kth term in the series. Equation 3 is not quite right because the first segment and the last segment $(N + 1)$ each contribute a Boltzmann factor to the overlapping pair and there should be only one factor. We correct this either by replacing the exponential factors in eq 4 by 1 or by replacing the last matrix in eq 3 by a matrix $\mathbf{W}_N$ which is equal to $\mathbf{W}$ except that the exponential factors in the matrix are each replaced by 1. Thus for example

$$Q_D = \sum_{k=1}^{M} \mathbf{U}_k{}^{T}\mathbf{W}_N\mathbf{W}^{N-1}\mathbf{P}_k(0) \text{ (one dimension)} \tag{5}$$

We now argue that for a ring with indistinguishable monomers the partition function Q_I is given by

$$Q_I = Q_D/2(N + 1) \tag{6}$$

By shifting the monomer numbers along the ring (i.e. $n \rightarrow n + 1$ for $n < N + 1$, and $N + 1 \rightarrow 1$), we obtain a different sequence. Doing this $N + 1$ times, we obtain $N + 1$ different sequences, each of which was generated by the matrices of eq 3. Yet they correspond to only one shape. By labeling in the reverse direction and shifting, we get another $N + 1$ sequences that correspond to the one shape. This explains the factor of $2(N + 1)$. As before there are some special shapes that are not counted $2(N + 1)$ times: they are counted only $N + 1$ times. In d dimensions the situation is more complicated.[6]

Theory, Body Centered Cubic Lattice

In the original treatment of one-dimensional adsorption of a linear polymer onto a plane substrate[8] we made the observation that for the body centered cubic lattice (bcc) the partition function for d dimensions equaled $2^{(d-1)N}Q_D$ where Q_D was the partition function for one dimension. Thus we were able to solve the d-dimensional problem for this special lattice. We now show that for the bcc lattice we can solve the ring problem also in this manner. Let us do this in the context of the two-dimensional problem. For every step up or down there is a step to the left or right. Each sequence of up and down steps can be decorated by an arbitrary sequence of left and right steps. For a linear polymer there are 2^N ways to step left or right. For a ring the number of steps to the left must equal the number of steps to the right. There are $N!/[(N/2)!]^2$ ways to do this. Thus the partition function, $Q_D(d)$, for a d-dimensional bcc lattice is

$$Q_D(d) = (N!/[(N/2)!]^2)^{(d-1)}Q_D \tag{7}$$

and we have solved a meaningful three-dimensional problem!

Notice that, using Stirling's approximation, eq 7 introduces a factor $2^N/\sqrt{N}$ for each dimension perpendicular to the normal direction. This is in accord with previous results[9] derived from the continuum Gaussian approach (in three dimensions) which is valid in the weak adsorption limit. These results gave z^N for the number of configurations of a chain in space with both ends free, $z^N/\sqrt{N}$ for a chain with one end attached to a plane surface, $z^N/N^{3/2}$ for a chain with both ends in the surface but one end free to move relative to the other, and $z^N/N^{5/2}$ when the ends are on the surface and joined together. These results are independent of dimension except for the last one which is replaced by $z^N/N^{1+d/2}$. One also expects that these results are only weakly dependent on lattice type.

The number of configurations of a ring when it leaves the surface increases from $z^N/N^{5/2}$ to $z^N/N^{3/2}$. For a linear polymer the increase is from $z^N/\sqrt{N}$ to z^N. Thus in the weak adsorption limit there is a greater loss of entropy for the ring on adsorption than for a linear chain. However for strong adsorption one must solve eq 7 to assess the situation (eq 9 for other lattices).

Theory, Other Lattices

For other lattices a different approach allows us to formulate the problem. Let us solve this in the context of the three-dimensional simple cubic lattice. In eq 2 we replace $z(1 - a) = 4$ by a factor $(L + R + F + B)$, while $za/2$ is replaced by 1. L, R, F, and B are counting variables so that when the matrix multiplications of eq 1 are performed we obtain for the linear polymer

$$Q = \sum_{i,j,k,r} A_{ijkr}L^{i}R^{j}F^{k}B^{r} \tag{8}$$

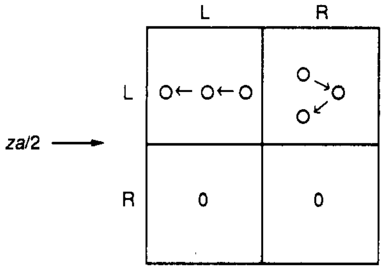
A factor L appears for each step to the left, a factor R for each step to the right, etc. The $za/2$ terms of the matrix allow for stepping up or down, the term to the left of the diagonal corresponding to a step toward the first layer. The generic term of eq 8 denotes that i steps were taken to the left, j to the right, k forward, and r backward, and these numbers are arbitrary integers for a linear polymer. The remaining $N - i - j - k - r$ steps are perpendicular to these layers. Q is obtained by setting $L = R = F = B = 1$. A ring has the condition that $i = j$ since the number of steps to the left must equal the number to the right, and also $k = r$ since the number of forward steps must equal the number of backward steps in order for the beginning and end points to coincide. These conditions plus eqs 4, which ensure that the chain begins and ends in the same level, ensure that the two chain ends superpose.

$$Q_D(\text{sc}) = \sum_{i,k} A_{iikk}L^{i}R^{i}F^{k}B^{k} = \sum_{i,k} A_{iikk} \tag{9}$$

Other lattices are easily handled in the same way. Thus we have succeeded in transcribing the ring problem into one of pure mathematics via eqs 7–9. Given the functional forms for Q and $Q_D(\text{sc})$, one now needs to determine the coefficients of the power series (right hand side).

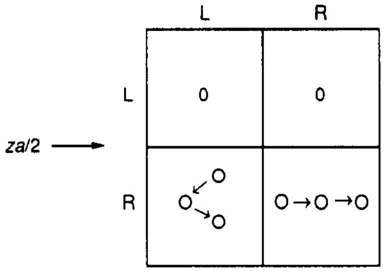
Theory, Chain Stiffness

In the 1971 paper on a linear polymer between plates the results for a polymer with chain stiffness was quoted in the context of the three-dimensional simple cubic lattice.[7] The ring problem introduces a few complications. So we now do the problem for the ring in the context of the simpler one-dimensional problem. The generalization to d-dimensions is straightforward. To solve our problem, we need to replace each of the entries of the matrix of eq 2 by a 2×2 matrix. This is done in two steps. First, we write down an "instruction matrix" where each of the elements of the matrix is a figure representing an instruction. Zero means do nothing. Then we replace the figures by numbers to obtain our final matrix. We have M equally spaced points on a line labeled from 1 to M sequentially beginning from the right. In eq 2 the $za/2$ term on the left off-diagonal is replaced by the 2 × 2 instruction matrix.



left off-diagonal (10)

The $za/2$ term on the right off-diagonal is replaced by



right off-diagonal (11)

while the $z(1-a)$ term is replaced by zero (each of the four elements of the matrix is zero). The new matrix **W** is now a $2M \times 2M$ instruction matrix. Each nonzero matrix element is a figure of two steps. The direction of the first step is given by the column label and the direction of the second step is given by the row label. Thus, the symbol represented by RL means step to the right and then step to the left. If the 2 × 2 matrix is in the fourth row and third column, then the second step corresponds to a step (to the left) from level 3 to level 4, and the first step was a step from 4 to 3. The stiffness energy represented by the weighting factor $\exp(\phi_S)$ is for stepping in the same direction while $\exp(\phi_B)$ corresponds to a reversal. Thus, the energy is associated with the angle between the two bonds. One multiplies two matrices together by the usual rules. "Multiply" means place the figure of the right matrix onto the figure of the left matrix so that the second bond of the figure taken from the right matrix superimposes on the first bond of the figure of the left matrix. Thus each time one multiplies from the left, one is adding one monomer and accounting properly for the stiffness energy. It is simple, but tedious, to show that matrix multiplication correctly generates all of the possible shapes of the chain.

We wish not only to generate each shape correctly but also to give them each a proper Boltzmann weight. This is done by placing the number $\exp(\phi_S)$ wherever the two steps are in the same direction (i.e. LL or RR) and by placing the number $\exp(\phi_B)$ wherever a LB or a BL appears. We thereby convert our matrices from symbolic to numerical matrices, but we now know what they mean. Thus our final numerical matrix **W** is given by eq 2 with the substitutions

$$za/2 \rightarrow \begin{bmatrix} \exp(\phi_S) & \exp(\phi_B) \\ 0 & 0 \end{bmatrix} \text{ left off-diagonal} \qquad (12)$$

$$za/2 \rightarrow \begin{bmatrix} 0 & 0 \\ \exp(\phi_B) & \exp(\phi_S) \end{bmatrix} \text{ right off-diagonal} \qquad (13)$$

The matrix **W** correctly places the third and all subsequent segments and gives them the proper weight. But, we need to treat the first and second segments differently. If we begin our chain at the kth level, then the first segment is accounted for by $\mathbf{P}_k(0)$ which is given by zeros everywhere except in the kth place. If the kth place is not at the surface, we have the components $^1/_2, ^1/_2$, if $k = 1$ we have $(^1/_2)\exp(\theta_1), (^1/_2)\exp(\theta_1)$, and if $k = M$ we have $(^1/_2)\exp(\theta_M), (^1/_2)\exp(\theta_M)$. If we allow the first segment freedom to start at every level then $\mathbf{P}(0)$ is given by

$$\mathbf{P}^{\mathrm{T}}(0) = (^1/_2 \exp(\phi_1),\ ^1/_2 \times \exp(\phi_1);\ ^1/_2, ^1/_2;\ ^1/_2, ^1/_2; \ldots;\ ^1/_2, ^1/_2;\ ^1/_2 \exp(\phi_M), ^1/_2 \exp(\phi_M)) \qquad (14)$$

The second segment is given by multiplying by the **W** of eq 2 with the substitution from eqs 12 and 13 except that the exponentials of eqs 12 and 13 are replaced by 1's. We call this new matrix $\mathbf{W}_1$. In this way we correctly account for adsorption energy of the second segment but do not allow a stiffness energy since two monomers alone do not determine a stiffness. One needs three consecutive monomers to determine a stiffness energy, and the stiffness energy is associated with the central monomer.

The partition function for a linear chain of $N + 1$ monomers constrained to M levels is given by

$$Q(M,N+1) = \mathbf{U}^{\mathrm{T}}\mathbf{W}^{N-1}\mathbf{W}_1\mathbf{P}(0) \qquad (15)$$

Notice that for a linear chain the number of flexes is 2 less than the number of monomers.

For a ring the number of flexes equals the number of monomer units. Consider the following quantity

$$Q_{\mathrm{D}} = \sum_k \mathbf{U}_k^{\mathrm{T}}(0)\mathbf{W}^N\mathbf{P}_k(0) \qquad (16)$$

Where $\mathbf{U}_k$ has 1's at the kth level and zeros elsewhere. $\mathbf{P}_k$ starts the chain at the kth level and $\mathbf{U}_k^{\mathrm{T}}$ places the $(N + 1)$th monomer on top of the first monomer laid down. For a linear chain these count as different monomers but for a ring they are really only one monomer. Thus we must not count the adsorption energy twice. We can do this either by replacing the exponential in $\mathbf{P}(0)$ by 1's or by replacing the exponential representing adsorption energies by 1's in the last matrix **W**. Call this new matrix $\mathbf{W}_N$. Then we have

$$Q_{\mathrm{D}} = \sum \mathbf{U}_k^{\mathrm{T}}(0)\mathbf{W}_N\mathbf{W}^{N-1}\mathbf{P}_k(0) \qquad (17)$$

This expression is the correct one for a ring of N monomers. In the linear case the first matrix $\mathbf{W}_1$ does not carry a flex energy because segments 1 and 2 cannot determine a stiffness energy, but in the ring case the monomers N, 1 (also labeled $N + 1$), and 2 determine a flex energy at their vertex. This energy is properly accounted for by using **W** rather than $\mathbf{W}_1$ for the first matrix.

Our result then is that eq 15 solves the problem of a linear polymer confined to M layers when both adsorption within the layers and stiffness energy within the chain are taken into account. Equation 17 solves the corresponding problem for a ring of N monomers.

These formulas also hold for the simple cubic lattice with the matrices appropriate to that problem being given in ref 7. In this case there are three different energies; straight line, ϕ_S; back-folding, ϕ_B; and 90° bends, ϕ_L. Other lattices are also easily treated.

We could if we wanted also account for orientation forces by introducing a factor $\exp(\psi_L)$ ($\exp(\psi_R)$) whenever we have a step to the left (right). The first factor would multiply every element of the L row, and the second factor, every element of the R row.

The method outlined above can also be used when the stiffness energy depends on the quadruplet of consecutive monomers rather than just a triplet. First, in building up the matrix, one labels the rows and columns by the 2-tuple number describing the orientations of the last two bonds of the three bond figures that constitute the elements of the symbolic matrix. For example instead of L (left) and R (right) as labels we would have LL, LR, RL, and RR. Second, the first two bonds of the figures are labeled by the column index and the last two bonds are labeled by the row index. Third, in multiplying the figures of the left matrix by those of the right matrix one superimposes the last two bonds of the right figure onto the first two bonds of the left figure. These three rules ensure that all possible polymer shapes are generated by symbolic multiplication.

Summary

We have solved the problem (calculated the partition function) of a polymer ring on a lattice of M layers. The method can be applied to any kind of lattice. We have worked in the context of the body centered cubic and the simple cubic lattices. The method allows for adsorption energies within any of the layers although explicit formulas were given only for adsorption to the first and last layers (surface adsorption). Simultaneous with adsorption, we have treated the problem of stiffness energy when stiffness energy depends on the angle between pairs of bonds. The case where the stiffness energy is associated with a triplet of bonds rather than a doublet is described. Energies that are dependent on single bond orientation are trivially included.

The solution to the isolated ring problem is a prerequisite for solving bulk ring systems.

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