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A microscopic model for ordered chain systems

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A microscopic model for a system of ordered chains is presented. The statistics of a single chain is calculated in a quadratic mean field potential that approximates the steric repulsions between the hydrocarbon chains. The partition function of the problem that contains long range interaction between segments, is transformed to a mathematically tractable Markovian form. Statistical averages and correlations are calculated showing a constant chain alignment near the interface that decays only towards the end of the chain.

I. INTRODUCTION

The statistical shape of a polymer chain is determined by the short range monomer-monomer interaction, and by nonbonded polymer-polymer (or polymer-solvent) interactions. The short range interaction determines the primary structure of the macromolecule, while its shape is determined usually by the nonbonded interactions. In general, the most probable shape is either an isotropic three-dimensional random coil, or a distribution about a preferred axis in space, which may be viewed as an array of quasi-one-dimensional objects. Examples of such quasi-one-dimensional systems are: nematic, smectic, and cholesteric liquid crystals,^{1,2} bilayers of lipid molecules, and biological membranes which are made up of them.³ Liquid crystals usually consist of fused aromatic rings and flexible chains; steric constraints, imposed by the rigid rings of neighboring molecules, limit the number of energetically feasible rotational isomeric states of the chain, resulting in a rodlike shape of the molecule. The chain is aligned about the long molecular axis, and this property is maintained in both the ordered and isotropic phases.

Biological bilayers consist of phospholipid molecules with polar head groups and tails of hydrocarbon chains. The head groups are constrained to lie approximately on a two-dimensional surface at an interface between an aqueous medium and a region of space containing the hydrophobic hydrocarbon chains. The highly correlated head groups play a similar role to that of the rigid rings in liquid crystals by imposing steric constraints on the chains. As a function of temperature and density of the head groups, phospholipid bilayers exhibit an order-disorder phase transition of the hydrocarbon chains.⁴⁻⁹ The ordered phase exhibits a quasi-one-dimensional structure with a characteristic long range order along the chain. At high enough temperature, where the probability of *gauche* rotations about the C-C bonds overcomes the chain-chain steric repulsions, cooperative melting of the chains to a disordered phase occurs. The transitions take place at temperatures of prime importance for biological systems.

Over the last years intensive research efforts have been performed in the hope of elucidating the properties of the ordered chains. Bulk properties were studied using calorimetric,⁵ spin resonance,⁶ light scattering,¹⁰ and x-ray diffraction⁸ techniques, resulting in information on the nature of the order-disorder phase transi-

tion. Information on the microscopic molecular level is mainly provided by deuterium NMR measurements.¹¹⁻¹⁴ Their main observation is that the quadrupolar splittings, for deuterium in CD₂ groups of the chains, are nearly the same for the first segments, and they decrease monotonically to zero towards the end of the chains. Thus, a chain may be characterized by an order parameter that remains constant for a finite region of the chain, and decreases to zero at its end. In addition, in the NMR experiments the normal to the interface is found to be an axis of symmetry of the chain. This observation disregards the existence of a cooperative tilting of chains near the interface. It should be noted that in ESR experiments a nonzero angle of tilt has been found.¹⁵ The source of the discrepancy may arise from the large size of the electron spin probe that may perturb the bilayer. The theoretical treatments of the problem are based on an Hamiltonian containing the short range intrachain monomer-monomer interaction, and interchain excluded volume repulsions and longer range attractions. The most difficult part of the problem is the treatment of the interchain interactions that determine the quasi-one-dimensional nature of the problem. The existing theoretical models overcome this difficulty by using various approximation schemes. One approach is to approximate the problem by lattice models. Along this line, Nagle¹⁶ constructed two-dimensional lattice models, reflecting the excluded volume interactions between the chains and the energies associated with the formation of *gauche* bonds. The model did not include head groups and density dependent van der Waals interaction hold the chains together. The lattice models were transformed to solvable dimer models, predicting first or second order phase transitions, depending on the details of the lattice models. Scott¹⁷ formulated a similar model containing hard core repulsions and weak attractive forces between molecules. The existence of the van der Waals interaction was crucial for the appearance of the order-disorder phase transition. Jacobs, Hudson, and Andersen¹⁸ treated a similar Hamiltonian using a scaled particle theorylike approach to describe the statistics of the interchain steric repulsion. In their approach, the whole system interacts with any given chain through the average lateral pressure which is proportional to density of the head groups. They used the experimentally known transition temperatures to adjust the parameters of their model. By analogy to the Maier-Saupe model for nematic liquid crystals Marcelja¹⁹ and Jähnig²⁰ used the

orientational part of the van der Waals intermolecular attractions to calculate, in the molecular field approximation, the chain anisotropy in the bilayer. It has been pointed out by Wulf²¹ that in aliphatic hydrocarbon chains the anisotropy of the attraction is much too small to affect the order significantly, and the chain anisotropy is mainly determined by the interchain steric repulsions. Consistent with this argumentation the lattice model of Dill and Flory²² treats the packing of short chains in a monolayer. The model assumes constant monomer density in the monolayer which imposes constraints on the configurations of the chains, resulting in a constant order parameter near the polar heads in agreement with the NMR experiments.¹¹⁻¹⁴ Terminations of chains in a layer parallel to the interface increase the probability of lateral placements in the next layer and additional terminations are enhanced. Thus, the model predicts a very fast decay of the order parameter towards the end of the monolayer that underestimates the experimental degree of order.

In this paper, we propose a microscopic model for bilayers based on the interchain steric repulsions. We consider a chain in a quadratic mean field potential due to its neighbors. This particular representation of the repulsive potential enables us to reduce considerably the complexity of the statistical problem. The partition function of the problem, that contains long range interactions among the various segments, is transformed to an equivalent Markovian form. The resulting nearest neighbors type partition function can be handled easily to obtain statistical averages and, in particular, the degree of order in the chain.

II. THE MODEL

We consider a layer of identical chains whose head groups are constrained to lie on a two-dimensional surface. For a high density of head groups, a change in the orientation of one chain attached to one of the head groups strongly affects, through steric repulsions, the rest of the chains. Therefore, we approximate the interchain interactions by a mean field approximation, where each chain lies in the mean molecular field of the rest of the chains. The position of the head group of a specified chain is defined to be the origin, and the z axis is defined to be perpendicular to the interface surface. The internal energies and the corresponding conformations of an alkyl chain are usually approximated by the three isomer state model.²³ The bond length and the valence angle between successive bonds are fixed, while the energy is a function of the azimuthal angle that has three possible minima defining three possible states. For simplicity, we project this model on a two-dimensional lattice. The chain is described by a walk on a square net lattice which form the xz plane. For each lattice point, the walk may proceed downward (the projection of the *trans* state) or leftward and rightward (the projection of the two symmetrical *gauche* states). The upward walk which does not have a three-dimensional isomer state analog is excluded. Each segment of the chain is associated with spin $S_i = 1$ with components: rightward = +1, leftward = -1, and downward = 0. Since cooperative tilting is excluded the ground state of the

system is the all *trans* one, and the steric repulsions are proportional to deviations from this configuration, i.e., to lateral placements in the x direction. We approximate the interchain interaction by a quadratic mean field potential. Thus, each segment is in a harmonic field, which tends to localize it along the main axis. The statistics of the chain becomes equivalent to the problem of a two-dimensional walk in a parabolic potential field. A chain of N segments is characterized by the Hamiltonian

$$H = J \sum_{i=1}^N x_i^2 + \sum_{i=1}^{N-1} E(S_i, S_{i+1}), \quad (\text{II.1})$$

where x_i is the distance of the i th segment from the z axis and J is the strength of the restoring mean field. The second term on the right-hand side of Eq. (II.1) represents the short range monomer-monomer interaction. The partition function is

$$Z_N = \sum_{\{S_i\}} \exp \left\{ -\beta \left[J \sum_i x_i^2 + \sum_i E(S_i, S_{i+1}) \right] \right\}, \quad (\text{II.2})$$

with

$$\beta = 1/kT.$$

Now x_i is equal to the sum of the spin components of all previous segments

$$x_i = \sum_{j=1}^i S_j. \quad (\text{II.3})$$

Let θ be a step matrix defined by

$$\theta_{ij} = \begin{cases} 1, & j \leq i \\ 0, & j > i \end{cases}, \quad (\text{II.4})$$

then x_i is given by the unrestricted sum

$$x_i = \sum_{j=1}^N \theta_{ij} S_j. \quad (\text{II.5})$$

The first term in the Hamiltonian becomes

$$J \sum_{i=1}^N x_i^2 = J \sum_{j,k=1}^N S_j S_k \sum_{i=1}^N \theta_{ij} \theta_{ik} = J \sum_{j,k=1}^N S_j S_k A_{jk}, \quad (\text{II.6})$$

where

$$A_{jk} = N + 1 - \frac{1}{2} [(j+k) + |j-k|]. \quad (\text{II.7})$$

The bilinear form of Eq. (II.6) exhibits the quadratic dependence of the mean field potential, and the symmetric coupling matrix A reflects the long range character of the problem. The next step in the evaluation of the partition function is based on the identity²⁴

$$\exp(-\frac{1}{2} \xi \cdot F \cdot \xi) = \frac{1}{C} \int_{-\infty}^{\infty} \cdots \int \exp(-\frac{1}{2} \tilde{y} \cdot F^{-1} \cdot y) \times \exp(i\sqrt{2} \xi \cdot y) dy_1 \cdots dy_N, \quad (\text{II.8})$$

where ξ is a column vector, F is a real symmetric non-singular matrix, and $C = \sqrt{(2\pi)^N \det(F)}$. The inverse of the coupling matrix A is a tridiagonal matrix obeying

$$A_{jk}^{-1} = 2\delta_{j,k} - \delta_{j,k+1} - \delta_{j,k-1}, \quad (\text{II.9})$$

$$A_{11}^{-1} = 1, \quad (\text{II.9a})$$

and $\det(A) = 1$. As a result of the tridiagonal nature of A^{-1} , the partition function factors into a simple product

form

$$Z_N = \left(\frac{1}{2\pi}\right)^{N/2} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} dy_1 \cdots dy_N \exp\left(-\frac{1}{2} y_N^2\right) \times \exp\left[-\frac{1}{2} \sum_{i=1}^{N-1} (y_i - y_{i+1})^2\right] \sum_{\{S_i\}} \prod_{i=1}^N \exp(\sqrt{2K} y_i S_i) \times \exp[-\beta E(S_i, S_{i+1})], \quad (\text{II. 10})$$

where $K = \beta J$.

For the special case $E(S_i, S_{i+1}) = 0$ for all the spin components, it is easy to perform the summation over the configurations $\{S_i\}$ and Eq. (II. 10) reduces to

$$Z_N = \left(\frac{1}{2\pi}\right)^{N/2} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} dy_1 \cdots dy_N \exp\left(-\frac{1}{2} y_N^2\right) \times \prod_{i=1}^N [1 + 2 \cos(\sqrt{2K} y_i)] \prod_{i=1}^{N-1} \exp\left[-\frac{1}{2} (y_i - y_{i+1})^2\right]. \quad (\text{II. 11})$$

The existence of the free damping term $\exp(-1/2 y_N^2)$ in Eqs. (II. 10) and (II. 11), reflects the fact that the first segment is connected to a fixed head group at the interface.

It should be noted that a similar reduction of a partition function occurs in Kac's one-dimensional model.²⁵ The model that describes a chain of N spins interacting via attractive potential of the form

$$H_{ij} = -J\gamma \exp(-\gamma|i-j|S_i S_j) \quad (\text{II. 12})$$

has a Markovian nature. As a result, its partition function is transformed to a nearest neighbors like form, formally similar to Eq. (II. 10). In the limit, $\gamma \rightarrow 0$, i. e., very broad interaction potential, the system has a phase transition at $K = \frac{1}{2}$ from a disordered phase to an ordered one.

III. RESULTS

The main qualitative features of the model are independent of the details of the short range monomer-monomer interaction. Therefore, we adopt the simplest case of Eq. (II. 11). By performing successive integrations over the variables y_1, y_2 and using the equalities (A1), (A6) (see the Appendix), one obtains a set of relations among the partition functions Z_N, Z_{N-1}, \dots :

$$Z_N = Z_{N-1} + 2 \exp(-K) Z_{N-2} + O[\exp(-2K)] \quad (\text{III. 1a})$$

$$Z_N = Z_{N-1} + 2 \exp(-K) Z_{N-2} + 2 \exp(-2K) Z_{N-3} + O[\exp(-3K)] \quad (\text{III. 1b})$$

$$Z_N = Z_{N-1} + 2 \exp(-K) Z_{N-2} + 2 \exp(-2K) Z_{N-3} + 2 \exp(-3K) [1 + \exp(-3K)] Z_{N-4} + \cdots \quad (\text{III. 1c})$$

Integration over a scalar at the j th step results in Z_{N-j} , while a $\cos(m\sqrt{2K} y)$ term adds a factor of $\exp(-Km^2)$ and couples to the next term to form $m, m \pm 1$ cosine terms. Thus, at each step the coefficient of Z_{N-j} is the sum of all possible contractions to form a scalar. Due to the fast convergence to zero of the exponents (for nonvanishing K), few terms are sufficient to calculate Z_N . At the thermodynamic limit $Z_N = \lambda Z_{N-1}$, where λ is a constant independent of N . Substituting this relation Eqs. (III. 1) reduce to polynomials in λ , and the partition function, obeying $Z_N \sim \lambda^N$, is deter-

TABLE I. Values of eigenvalues determining Z_N from solution of polynomials with $2 < m < 5$ for various K values.

K	λ_2	λ_3	λ_4	λ_5	λ_{exact}
0	2	2.27	2.436	2.537	3
0.5	1.709	1.863	1.913	1.931	
0.75	1.593	1.707	1.737	1.745	
1	1.493	1.577	1.595	1.598	
1.5	1.334	1.378	1.384	1.385	
2.0	1.222	1.244	1.244	1.244	
∞	1	1	1	1	1

mined by the largest root of a low order polynomial of the form

$$\lambda^m + \sum_{j=0}^{m-1} a_j \lambda^j = 0. \quad (\text{III. 2})$$

The order of the truncation m is determined by K . In Table I, values of λ for various K are given for different orders of truncation. Except for the extreme case $K \sim 0$ λ_m converges for $m < 5$. Since $a_j < 0$ for all j the set of largest roots λ_m form a sequence of successively improving lower bounds to λ . As usual, the free energy per segment is given by

$$-\frac{\beta F}{N} = \ln \lambda, \quad (\text{III. 3})$$

which is bound between zero (zero temperature limit) and $\ln 3$ (high temperature limit). The roots of the polynomial (III. 2) are equal to the eigenvalues of the symmetric infinite transfer matrix $T(x, y)$ defined by

$$T(x, y) = \frac{1}{\sqrt{2\pi}} [1 + 2 \cos(\sqrt{2K} y)]^{1/2} \times [1 + 2 \cos(\sqrt{2K} x)]^{1/2} \exp\left[-\frac{1}{2} (x - y)^2\right]. \quad (\text{III. 4})$$

The negativity of all the a_j 's implies that λ is the only real positive eigenvalue of T . Thus, degeneracy of the largest eigenvalue does not occur for all K , indicating that a phase transition does not exist.²⁶ The alignment along the chain is exhibited by $\langle S_j^2 \rangle$ the weight of lateral placement at the j th segment defined by

$$\langle S_j^2 \rangle = \frac{1}{Z_N} \left(\frac{1}{2\pi}\right)^{N/2} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} dy_1 \cdots dy_N 2 \cos(\sqrt{2K} y_j) \times \exp\left(-\frac{1}{2} y_N^2\right) \prod_{i=1}^N [1 + 2 \cos(\sqrt{2K} y_i)] \times \prod_{i=1}^{N-1} \exp\left[-\frac{1}{2} (y_i - y_{i+1})^2\right]. \quad (\text{III. 5})$$

Using Eqs. (A. 1) and (A. 6) one obtains

$$\langle S_1^2 \rangle = \frac{2 \exp(-K)}{\lambda^2 - \lambda \exp(-K) - \exp(-5K)} + O[\exp(-9K)], \quad (\text{III. 6a})$$

$$\langle S_2^2 \rangle = \langle S_1^2 \rangle \left[1 + \frac{1}{\lambda} [1 - \exp(-K)]\right], \quad (\text{III. 6b})$$

$$\langle S_3^2 \rangle = \langle S_1^2 \rangle \left\{ \frac{1}{\lambda} + \frac{1}{\lambda^2} [1 + \exp(-K) + \exp(-5K)] \right\} + \frac{2 \exp(-2K)}{\lambda}. \quad (\text{III. 6c})$$

For all nonvanishing K , $\langle S_1^2 \rangle$ is smaller than the other self-correlation terms $\langle S_j^2 \rangle$, reflecting the lack of freedom due to its immediate vicinity to the polar head.

TABLE II. Values of $\langle S_j^2 \rangle$ as a function of K .

K	$\langle S_1^2 \rangle$	$\langle S_2^2 \rangle$	$\langle S_3^2 \rangle$	$\langle S_4^2 \rangle$
0.5	0.486	0.574	0.560	0.560
0.8	0.417	0.541	0.529	0.531
1.0	0.374	0.512	0.500	0.503
1.2	0.334	0.480	0.469	0.471
1.5	0.277	0.433	0.415	0.416
1.8	0.226	0.362	0.358	0.359
2.0	0.196	0.332	0.320	0.321
2.2	0.168	0.293	0.283	0.284
2.5	0.133	0.238	0.231	0.231
3.0	0.087	0.162	0.159	0.159

For the entire temperature range $\langle S_j^2 \rangle$ is almost the same for all the monomers. At the low temperature limit, the probability of the *trans* configuration increases like $1 - 4 \exp(-K)$ for all segments (except the first one). Representative results of $\langle S_j^2 \rangle$ as a function of K are shown in Table II. The reduction of $\langle S_j^2 \rangle$ with K increases the chain alignment, and results in a stretching of the chain. The projection of the chain length along the z axis is given by

$$\langle z \rangle = \sum_{j=1}^N (1 - \langle S_j^2 \rangle). \quad (\text{III. 7})$$

The chain is stretched from $\frac{1}{3}N$ the value of the free chain to $N[1 - 4 \exp(-K)]$ for $K > 1$.

A system of finite chains at the high temperature limit exhibits some interesting features. The validity criterion for this limit is $KN^2 \ll 1$, $K \ll 1$ itself is not a sufficient condition for the high temperature limit since there are configurations with $Kx_i^2 > 1$. It is convenient to treat this limit by expanding the cosines in terms of y . The partition function is given by

$$Z_N = 3^N \left[1 - \frac{K}{3} N(N+1) \right] \quad (\text{III. 8})$$

and

$$\langle S_j^2 \rangle = \frac{2}{3} - \frac{2}{9} K(N+1-j). \quad (\text{III. 9})$$

Here, the increase in the freedom of a monomer is highly dependent on its distance from the polar head. At the end of the chain $j \sim N$ the flexibility is still retained, while near the interfacial surface the reduction in the chain flexibility is more substantial. The average stretching per segment is N dependent

$$\frac{\langle z \rangle}{N} - \frac{1}{3} = \frac{2}{9} K(N+1). \quad (\text{III. 10})$$

The pair correlation between segments that measures the relative tendency to be in *gauche* states is independent of the separation $|j-i|$ between the segments and entirely depends on the distance of the last segment from the end of the chain

$$\langle S_i S_j \rangle = -\frac{8}{9} K(N+1-j) \quad (\text{III. 11})$$

and

$$j = \max(i, j).$$

The minus sign results from the fact that each (\pm) ro-

tation is likely to be followed by an opposite (\mp) rotation. The existence of a boundary condition, in the form of a polar head anchored at the interface, has in this limit a very strong effect on the chain, which is reflected in the lack of translational invariance of the pair correlation function. It should be noted again that this high temperature regime is limited to finite chains fulfilling the condition $KN^2 \ll 1$.

IV. DISCUSSION

The model presented here predicts some interesting properties of ordered chains. The anisotropy in the bilayer is attributed to interchain steric repulsions represented by a restoring mean field potential. The main result of the model is the prediction of a constant alignment along the chain. This result is compatible with the NMR experiments¹¹⁻¹⁴ showing a constant quadrupolar order parameter for most of the segments. The uniform decrease in freedom results in a net stretching of the chain along the normal to the interface with $\langle \Delta z \rangle$ proportional to N . A similar behavior has been found by de Gennes²⁷ and Alexander²⁸ using scaling arguments based on the boundary conditions on the chains together with the requirement that the density be constant. The existence of a fixed polar head imposes alignment on the chain even at the high temperature limit. This property is exhibited by the fact that K is not a relevant small parameter, and a high temperature expansion does not exist in the usual sense. Mathematically, its effect is manifested through the free damping term in the expression for the partition function.

The quadratic form of the mean field potential is essential in the reduction of the problem into a tractable form. Nevertheless, it seems that the qualitative features of the model are not too sensitive to the details of the mean field potential. Obviously, J the potential strength is intimately connected to the density of the polar heads. The main deficiency of the present model is the independence of J on z , the distance from the interface. The uniform field strength exaggerates the alignment at the chain's end.

The two-dimensional lattice projection of the chain is more sensitive to restrictions imposed on *gauche* states by the molecular field than the three-dimensional chain. A generalization to a three-dimensional model including interchain interactions can be done by describing the propagation of the chain by the Wigner rotation operators.^{29,30}

APPENDIX

The calculation of high and low temperature averages involves integration of various moments of Eq. (II.11). Some helpful recursion relations are derived here.

$$\begin{aligned} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp[-\frac{1}{2}(y_1 - y_2)^2] dy_1 \\ = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(\frac{1}{2}y^2) dy = 1. \end{aligned} \quad (\text{A1})$$

Thus, it is sufficient to start the integration process at

the first site (from the left) containing a power of y_i ,

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} y_i \exp\left[-\frac{1}{2}(y_i - y_{i+1})^2\right] dy_i = y_{i+1}. \quad (\text{A2})$$

As a result, $\langle y_i y_j \rangle = \langle y_{i+1} y_j \rangle = \langle y_j^2 \rangle$ independent of $|i-j|$ and i (we assume here that $j > i$)

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} y_i^2 \exp\left[-\frac{1}{2}(y_i - y_{i+1})^2\right] dy_i = 1 + y_{i+1}^2, \quad (\text{A3})$$

implying that $\langle y_{i+1}^2 \rangle = N+1-i$. In general,

$$\begin{aligned} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp[-c_1(y-a)^2 - c_2(y-b)^2] dy \\ = \frac{1}{\sqrt{2(c_1+c_2)}} \exp\left[-(a-b)^2 c_1 c_2 / (c_1+c_2)\right]. \end{aligned} \quad (\text{A4})$$

Using this relation one obtains for the n th moment (n even).

$$\begin{aligned} \langle y_j^n \rangle &= \left(\frac{1}{2\pi}\right)^{N/2} \int_{-\infty}^{\infty} \cdots \int dy_1 \cdots dy_N \exp\left[-\frac{1}{2} \sum_{i=1}^{N-1} (y_i - y_{i+1})^2\right] \\ &\times \exp\left(-\frac{1}{2} y_N^2\right) y_j^n = \frac{1}{\sqrt{2\pi} \sqrt{n+1-j}} \\ &\times \int_{-\infty}^{\infty} y^n \exp\left(-\frac{1}{2} y^2 / (n+1-j)\right) dy = (n-1)!! (N+1-j)^{n/2}. \end{aligned} \quad (\text{A5})$$

Integral involving cosines can be treated, too.

$$\begin{aligned} \int_{-\infty}^{\infty} \cos\sqrt{2k} y_i \exp\left[-\frac{1}{2}(y_i - y_{i+1})^2\right] dy_i &= \frac{1}{2} \exp(i\sqrt{2k} y_{i+1}) \\ &\times \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2} y^2 + i\sqrt{2k} y\right) dy + \text{c. c.} \\ &= \sqrt{2\pi} \exp(-k) \cos\sqrt{2k} y_{i+1} \end{aligned} \quad (\text{A6})$$

each integration over a cosine term shifts the cosine one step towards the end of the chain, and adds a factor of $\exp(-k)$.

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