Statistics of Chain Order in Interphases

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Introduction

In lipid bilayers (composed of n-alkyl chains with polar heads), the assembly of hydrocarbon chains evolves from a structure resembling lamellar crystallites at the hydrocarbon–aqueous phase interface to one more like an amorphous polymer in the bilayer interior. The two monolayers which compose the bilayer are similar to the interphase between crystalline and amorphous regions in semicrystalline polymers. The change in anisotropy of chain orientation in the interphase can be observed by NMR, for example.[1] Dill and Flory[2] proposed a lattice model for the interphase that provides a rationalization of the disorder gradient. The model of the bilayer (or of the monolayers which comprise it) is a series of layers of lattice points each occupied by a statistical segment of a hydrocarbon chain subject to a constraint of constant density in the (symmetrical) bilayer. This model constraint of complete occupancy of lattice sites is motivated by the hydrophobic effect which prevents the incorporation of water in the bilayer. Ignoring reversals, as seems appropriate for short and densely packed chains,[2] the model of Dill and Flory is characterized by the density of chain ends (σ) in the first layer and the number of statistical segments ($n + 1$) per chain. Typical values used by Dill and Flory to fit experimental determinations of the disorder profile were $\sigma = 0.66$ and $n + 1 = 5$.

In their analysis of the lattice model, Dill and Flory assumed that the passage of chains from one layer to the next conformed to a Markovian sequence, and they employed a matrix procedure for determining the probability of chain growth along (p_i) and orthogonal ($q_i = 1 - p_i$) to the normal to the bilayer in each layer i. The order parameter, which is related to experimental observables, is given by

$$S_i = \frac{1}{2}(3p_i - 1) = \frac{1}{2}\langle 3\cos^2\theta_i - 1\rangle$$

where θ_i is the angle between a chain and the bilayer normal in the ith layer. The brackets indicate an ensemble average. The molecular picture underlying the Dill and Flory model is that as chains terminate in each layer, filling subsequent layers requires more orthogonal moves and thereby S_i decreases with layer index, as required by the experimental results.

Since the initial paper of Dill and Flory,[2] a number of similar mean field theories have appeared, some not using a lattice.[3] A comprehensive mean field theory including reversals was developed by Naghizadeh and Dill.[4] All theories assume independent chain statistics.

However, this assumption is open to examination as the configuration of a given chain in the bilayer is controlled to some extent by the configuration of its neighbors. In addition, the small number of statistical segments in the chains, and the moderate (order tens) number of chains in the bilayer (here treated as symmetrical contacting monolayers) suggests some role of edge effects. We present an analysis of the intermolecular excluded volume effects and the edge effects for the Dill–Flory model employing direct enumeration of all allowed system configurations. The idea is to eliminate preaveraging and have individual chain growth controlled by the actual space instead of the average space available to the assembly of all chains.

Our analysis relates to the original model of Dill and Flory.[2] More elaborate models (for example allowing reversals) need not be considered to assess the role of configuration interaction and edge effects.

Table 1. Chain Growth Probabilities and Order Parameters (p_i, S_i)

i	1 × 3		2 × 3		3 × 3	
1	0.666 67	0.500 00	0.666 67	0.500 00	0.666 67	0.500 00
2	0.666 67	0.500 00	0.641 87	0.462 80	0.636 45	0.454 68
3	0.500 00	0.250 00	0.363 50	0.045 26	0.373 71	0.060 57

i	1 × 6		2 × 6	
1	0.666 67	0.500 00	0.666 13	0.499 19
2	0.650 00	0.475 00	0.638 29	0.457 44
3	0.414 63	0.121 95	0.368 73	0.053 09

i	1 × 9	
1	0.666 67	0.500 00
2	0.650 61	0.475 91
3	0.416 02	0.124 03

i	1 × 12	
1	0.666 67	0.500 00
2	0.649 98	0.474 97
3	0.413 27	0.119 91

i	1 × 15			Dill–Flory
1	0.666 67	0.500 00	0.663 80	0.495 70
2	0.649 82	0.474 73	0.629 06	0.443 58
3	0.411 48	0.117 23	0.357 47	0.036 20

Data Base

We choose $\sigma = {}^2/_3$ and $n + 1 = 5$. These numbers are close to those used by Dill and Flory to analyze experimental determinations of the order parameter gradient. For this choice of σ and n, the model requires that the first three layers be completely filled and the fourth layers be one-third filled. A simple calculation employing the matrix formulation of Dill and Flory yields values for p_i and S_i shown in Table 1.

When the system configurations are enumerated, additional parameters, the number and geometry of the lattice points in each layer, must be specified. The lattice model has each layer composed of a rectangular array of lattice points (here taken in multiples of three for convenience). With the bilayer normal in the z-direction, the smallest possible layer contains three lattice points in the x-direction (a 1 × 3 array). Larger layers are constructed by juxtaposition of this building block (i.e. 1 × 6, 1 × 9, ..., 2 × 3, 3 × 3, ...). Edge effects can be eliminated by forming sufficiently large two-dimensional arrays.

The 1 × 3 case is done easily by hand. Two chains emanate from the first layer. There are three ways of choosing the chain starting positions. Four distinct system configurations (consisting of two nonoverlapping chains in a (1 × 3) × 4 lattice) can be realized. The number of system configurations for larger layers grows rapidly and the bookkeeping was done by computer.

The general algorithm employed was as follows. Given J chains emanating from the first layer, the

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$\binom{3J/2}{J}$ distinct configurations of the chain starting positions in the first layer were generated (note that the 1 × 6 and 2 × 3 problems are topologically distinct and must be considered separately). (Since we chose $\sigma = {}^2/_3$ and the first layer is composed of 1 × 3 building blocks, J equals 2 times the number of 1 × 3 blocks in the first layer and J is always even. No special significance should be attached to this result.) All possible four-bond chains were constructed, and the computer placed chains successively on the starting positions and recorded successful attempts to generate acceptable system configurations (no chain overlap, complete occupancy of each layer except the last). For each chain type the number of forward and orthogonal moves in each layer was determined, and the results were multiplied by the total number of occurrences of each chain type in the collection of allowed system configurations. This scheme leads to values of p_i (i = 1−3) for each layer geometry. Some results are shown in Table 1. The results suffice to show the role of edge effects and to separate the influence of edge effects from the role of excluded volume. Characterization of larger arrays was prevented by limitations of computer power.[5]

Analysis

First Layer. Only the 2 × 6 case was large enough to allow chain termination in the first layer. Even so, chain termination in the first layer is a rare event and p_1 is close to ${}^2/_3$ for all the cases studied *and* for the Dill−Flory model. The first layer results are uninformative.

Second and Third Layers. With only four structures present, the 1 × 3 case cannot be included in a statistical study (all other cases contan tens to millions of structures). Little change in p_i is seen in going from 1 × 6 to 1 × 15, suggesting that edge effects in the long layer dimension have already vanished once the layer dimension becomes comparable to the number of statistical segments. The terminal value of p_3 of about 0.41 is larger than the Dill−Flory model value, but the 1 × n cases still contain edge effects in the short layer dimension. An additional reduction of p_i can be expected and is shown by going from the 1 × 6 to 2 × 6 cases. In fact, the 2 × 6 results (and the 3 × 3 results) are close to the Dill−Flory values, suggesting that intermolecular excluded volume effects are small and do not undermine the mean field approach. We conclude that edge effects vanish quickly with system size and that intermolecular excluded volume plays at most a very minor role in affecting the order parameter.

Although not quantitative, both the discrete enumeration calculations and the Dill−Flory scheme lead to the result that the natural logarithm of the number of system configurations is approximately proportional to the number of lattice sites in a layer.

References and Notes

(1) Stockton, G. W.; et al. *Nature* **1977**, *269*, 267.
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(4) Dill, K. A.; Naghizadeh, J. *Macromolecules* **1991**, *24*, 1768.
(5) Calculations were performed on a VAX cluster purchased under NSF grant number CHE-9007850.

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