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Molecular Model for Chain Ordering in Biomembranes†

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Detailed comparison between the self-consistent theory of nematic liquid crystals and membranes is made. A modified mean field Hamiltonian is so constructed as to take into account the connectivity of the chains and the constraints imposed due to the polar head surface. This gives rise to a variation of order parameter along the chain, which has been studied below the transition point. Results agree satisfactorily with experiment.

I. INTRODUCTION

In the past few years there have been a number of experimental investigations on segmental ordering in lipid bilayer chains.[1,2,3] The experiments were carried out mainly with deuterium magnetic resonance (DMR) and EPR by means of spin labels, where segmental order parameters were measured. The DMR results indicate that the order parameter remains constant over most of the chain and decreases rapidly towards the end.[1,2,3] On the theoretical side Marcelja[4] using a nematic model and computer simulation of chains in a lattice was able to predict the variation of order parameter along the chain.

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In lipid bilayer and natural membranes the basic units are not rigid molecules as in nematic liquid crystals, but segments of hydrocarbon chains. The orientation of segments are restricted since the valance bond angle remains constant and only three internal rotation angles are accessible. Marcelja has treated the hydrocarbon chain of the lipid molecules as consisting of a number of links which may assume arbitrary orientations. He adapted the mean field theory of nematic liquid crystals, Maier–Saupe theory, to the case of bilayer membranes.[4,5] Marcelja introduced an additional parameter η_0, which takes into account the special features of the membranes such as "lateral pressure," connectivity force between successive segments, boundary forces, smectic order parameter, etc.

In this report we attempt to present a theoretical model which explicitly includes the special features of bilayer membranes as distinguished from nematic liquid crystals. Applying the usual mean field approximation, we obtain expressions for the average mean order parameter of segments along the chain, self-consistently. The self consistent equations are solved numerically and the change of order parameter along the chain is investigated.

II. THE MODEL

Experimental evidence indicates that a bilayer is composed of short phospholipid chains with a dipole attached to a short polymer of approximately 16 to 20 carbon atoms. The dipole part of the chain is in contact with water–salt solution and forms a stable monolayer which is due to strong electrostatic forces, and can be considered as a permanent smectic layer. The first hydrocarbon bond emanating from the dipole is restricted in its orientations through the bonding forces and the succeeding bonds are likely to be influenced in their orientations in this manner. The bilayer is composed of two such systems placed upon one another with opposite orientations. We shall consider one of these monolayers for convenience. A realistic model of these systems must include the special structure of the first layer (the dipole smectic layer) and its influence on the succeeding layers through the bonding forces. The latter includes two separate contributions. The first is due to interchain segmental interactions, and the second the orientation correlation between succeeding links. Thus there is a distinct difference between nematic liquid crystalline and membrane systems due to con-

nectivity (of chains) and the boundary condition imposed by the first layer. The Hamiltonian for the system may be written as follows:

$$H = -\sum_{\alpha,\beta=1}^{n} I_{\alpha\beta}\eta_0^\alpha\eta_0^\beta - \sum_{\alpha,\beta=1}^{n}\sum_{i,j=1}^{N} J_{ij}^{\alpha\beta}\eta_i^\alpha\eta_j^\beta - \sum_{\alpha=1}^{n}\sum_{i=1}^{N} K_{i,i+1}^{\alpha}\eta_i^\alpha\eta_{i+1}^\alpha + H\sum_{\alpha=1}^{n}\sum_{j=1}^{N}\eta_j^\alpha \quad (1)$$

It is assumed that $J_{ij}^{\alpha\beta} = 0$ unless $i \neq j$ and $\alpha \neq \beta$, thus the interaction between the chains is included in the second term and interaction along the chain in the third term in Eq. (1). In this Hamiltonian the chains are denoted by Greek superscripts α and β running from 1 to n and the links of the chain are denoted by i and j running from 1 to N. η_i^α is the orientation measure for the link i of the chain α given by

$$\eta_i^\alpha = \frac{3}{2}\cos^2\theta_i - \frac{1}{2} \quad (2)$$

where θ is the angle of the link with the z axis (preferred axis of orientation).

The Hamiltonian (1) consists of several parts. The first term is assumed to be permanently smectic, therefore, the coupling constant I may be assumed to be large and η_0^α nonzeros and constants. This term, therefore, makes a constant contribution to the Hamiltonian. The third term in Eq. (1) is the contribution to the energy of orientational correlation between neighboring links. This contribution arises from the connectivity of the chain and is absent in homogeneous nematic liquid crystals. It has the form such that η_i of any link interacts with the neighboring link η_{i+1} along the chain. The last term in Eq. (1) denotes the contribution of external forces such as lateral pressure. This Hamiltonian is distinguished from the Hamiltonian of simple ordinary nematics by the presence of additional terms, chain connectivity, lateral pressure and the boundary layer.

III. THE MEAN FIELD APPROXIMATION

The mean-field approximation to Eq. (1) can be employed by using the following mean field criterion[6,7]

$$\begin{aligned}\eta_i^\alpha\eta_j^\beta &= \langle\eta_i^\alpha\rangle\eta_j^\beta + \langle\eta_j^\beta\rangle\eta_i^\alpha - \langle\eta_i^\alpha\rangle\langle\eta_j^\beta\rangle \\ \eta_i^\alpha\eta_{i-1}^\alpha &= \langle\eta_i^\alpha\rangle\eta_{i-1}^\alpha + \langle\eta_{i-1}^\alpha\rangle\eta_i^\alpha - \langle\eta_{i-1}^\alpha\rangle\langle\eta_i^\alpha\rangle\end{aligned} \quad (3)$$

and assuming $\langle \eta_i^\alpha \rangle = \langle \eta_i^\beta \rangle$, $\langle \eta_i^\alpha \rangle \neq \langle \eta_{i-1}^\alpha \rangle$ $J_{ij}^{\alpha\beta} = 0$ for $i \neq j$

$$J_{ii}^{\alpha\beta} = J_i^{\alpha\beta},\ K_{i,i+1}^{\alpha} = K_i^{\alpha} = K \text{ independent of } i \text{ and } \alpha$$

and

$$V_0 = 2 \sum_{\alpha} J_i^{\alpha\beta}, \quad \text{independent of } i \text{ and } \beta$$

we arrive at the following mean field Hamiltonian

$$H_{j\,\mathrm{MF}}^{\beta} = -\ \text{const.} - (V_0 \langle \eta_j \rangle - H)\eta_j^{\beta} + \frac{V_0}{2} \langle \eta_j \rangle^2 + [K][\langle \eta_j \rangle \eta_{j-1}^{\beta} + \langle \eta_{j-1} \rangle \eta_j^{\beta} - \langle \eta_j \rangle \langle \eta_{j-1} \rangle] \quad (4)$$

It is now possible to derive the hierarchy of self-consistent equations for the order parameter along the chain

$$\langle \eta_1 \rangle = \frac{\displaystyle\int_0^1 dx \left(\frac{3}{2}x^2 - \frac{1}{2}\right) \exp\left[\frac{V_0}{k_B T}\left(\langle \eta_1 \rangle - \frac{H}{V_0} - \frac{K}{V_0}(\langle \eta_0 \rangle + \langle \eta_2 \rangle)\right)\left(\frac{3}{2}x^2 - \frac{1}{2}\right)\right]}{\displaystyle\int_0^1 dx \exp\left[\frac{V_0}{k_B T}\left(\langle \eta_1 \rangle - \frac{H}{V_0} - \frac{K}{V_0}(\langle \eta_0 \rangle + \langle \eta_2 \rangle)\right)\left(\frac{3}{2}x^2 - \frac{1}{2}\right)\right]}$$

$$\langle \eta_j \rangle = \frac{\displaystyle\int_0^1 dx \left(\frac{3}{2}x^2 - \frac{1}{2}\right) \exp\left[\frac{V_0}{k_B T}\left(\langle \eta_j \rangle - \frac{H}{V_0} - \frac{K}{V_0}(\langle \eta_{j-1} \rangle + \langle \eta_{j+1} \rangle)\right)\left(\frac{3}{2}x^2 - \frac{1}{2}\right)\right]}{\displaystyle\int_0^1 dx \exp\left[\frac{V_0}{k_B T}\left(\langle \eta_j \rangle - \frac{H}{V_0} - \frac{K}{V_0}(\langle \eta_{j-1} \rangle + \langle \eta_{j+1} \rangle)\right)\left(\frac{3}{2}x^2 - \frac{1}{2}\right)\right]}$$

$$\langle \eta_N \rangle = \frac{\displaystyle\int_0^1 dx \left(\frac{3}{2}x^2 - \frac{1}{2}\right) \exp\left[\frac{V_0}{k_B T}\left(\langle \eta_N \rangle - \frac{H}{V_0} - \frac{K}{V_0}(\langle \eta_{N-1} \rangle + \langle \eta_{N+1} \rangle)\right)\left(\frac{3}{2}x^2 - \frac{1}{2}\right)\right]}{\displaystyle\int_0^1 dx \exp\left[\frac{V_0}{k_B T}\left(\langle \eta_N \rangle - \frac{H}{V_0} - \frac{K}{V_0}(\langle \eta_{N-1} \rangle + \langle \eta_{N+1} \rangle)\right)\left(\frac{3}{2}x^2 - \frac{1}{2}\right)\right]} \quad (5)$$

We shall note that the effective field seen by segment j of a chain with order parameter $\eta_j = \frac{3}{2}\cos^2\theta_j - \frac{1}{2}$ is:

$$H_{\text{eff}} = H - V_0\langle\eta_j\rangle + K(\langle\eta_{j-1}\rangle + \langle\eta_{j+1}\rangle) \tag{6}$$

IV. NUMERICAL COMPUTATION

The hierarchy of Eqs. (5) have three parameters: (a) temperature which appears as V_0/k_BT, (b) a parameter related to lateral pressure H/V_0, in this case one could show that $H \sim PA$, A being the area per unit head and P the lateral pressure, (c) the third parameter, K/V_0, is a measure of nearest neighbor correlation of the order parameter which is consequence of chain connectivity. Whereas the parameters described in (a) and (b) appear in earlier theories, the connectivity parameter K is a peculiarity of the present model. We attempt in our computation to choose suitable values of the three parameters in order to produce the experimental results of Seelig and Niederberger; further the results should reasonably be in agreement with numerical work of Marcelja. Since the hierarchy of equations are nonlinear there is a narrow range of K which gives a decreasing function of order parameter along the chain at $H = 0$ ($P = 0$). The shape of our decreasing curve at $K = -.145$ differs from that of Marcelja at $H = 0$. However, there is no experimental measurement at $P = 0$ in order to verify the correctness of

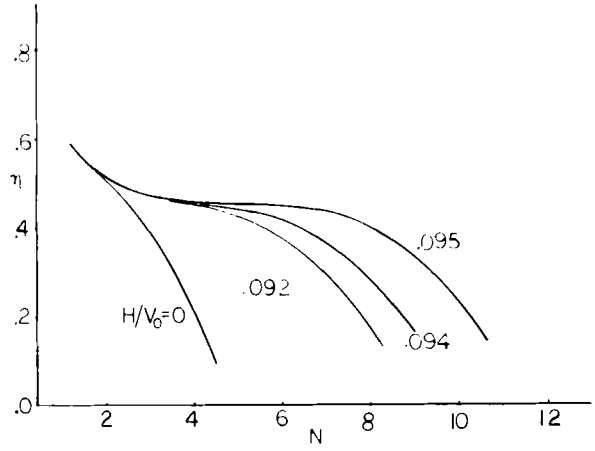

FIGURE 1 Variation of order parameter $\langle\eta\rangle$ along the chain as a function of H/V_0 (~lateral pressure) at $V_0/k_BT = 3.6$.

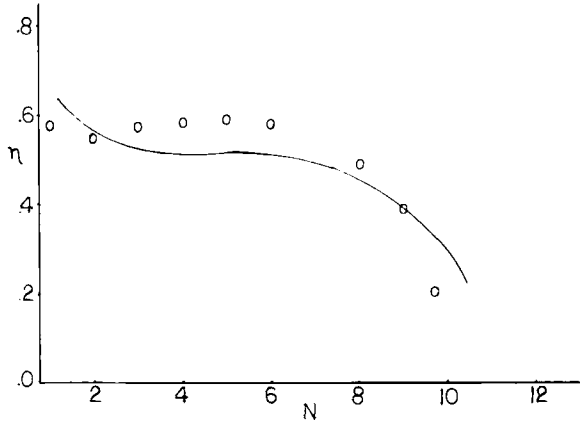

FIGURE 2 Variation of order parameter $\langle\eta\rangle$ along the chain at $H/V_0 = .095$ and $V_0/k_BT = 3.6$. The circles denote the experimental points obtained by Seelig and Niederberger.[1]

either curve. Actually a different choice of K within the range where there is a decreasing function of order parameter along the chain, does not alter the shape of the curve (at nonvanishing P) significantly. As for the choice of temperature we choose $V_0/k_BT = 3.6$. This value corresponds to the nematic phase of liquid crystals. Figure 1 shows the change of the order parameter along the chain as a function of H (lateral pressure). Of these the most significant curve is that corresponding to $H/V_0 = 9.5 \times 10^{-3}$ and $V_0/k_BT = 3.6$, which agrees quite well with the experimental curve of Seelig and Niederberger shown in Figure 2. Figure 3 shows the logarithmic variation of the order parameter along the chain for $H/V_0 = 9.5 \times 10^{-3}$ and $H/V_0 = 9.4 \times 10^{-3}$ and $V_0/k_BT = 3.6$ which has similar features as the curve obtained by

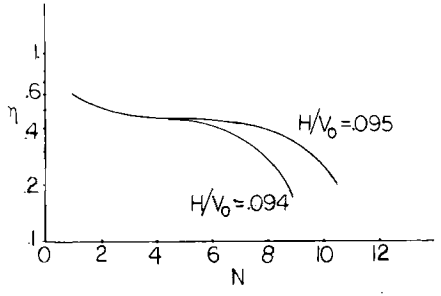

FIGURE 3 Logarithmic variation of order parameter $\langle\eta\rangle$ along the chain for $H/V_0 = .095$ and $H/V_0 = .094$, at $V_0/k_BT = 3.6$.

Henriksson *et al.*[3] The dependence of order parameter on lateral pressure ($\sim H$) agrees with observations by Mely *et al.* in that decreasing H decreases the value of order parameter and narrows the plateau region.

V. CONCLUSION

In this note we have extended the nematic model of liquid crystals developed by Marcelja, to include the special features due to chain connectivity of the nematic segments. Macelja's model for variation of order parameter along the chain is based on a simulation of chains in a lattice and therefore is difficult to carry out and the physical agency causing the variation of the order parameter along the chain is not transparent. We have attempted a simple mean field model in which this effect is naturally included as a consequence of chain connectivity. The results obtained are in satisfactory agreement with the available experimental data. However, the system of Eqs. (5) suffers from the disadvantage that since the number of independent parameters in the exponent (H, T, K and the initial values) is large and the equations are highly nonlinear, the range of variables which yield physically meaningful results is limited to a narrow region. In other words the equations are stable only within a narrow range of variables. Further investigation is necessary in this area.

References

1. J. Seelig and W. Niederberger, *Biochemistry*, **13**, 1585 (1974).
2. J. Charvolin, P. Manneville and B. Meloche, *Chem. Phys. Lett.*, **23**, 345 (1973).
3. U. Henriksson, L. Odberg and J. C. Eriksson, *Mol. Cryst. Liq. Cryst.*, **30**, 73 (1975).
4. S. Marcelja, *Biochem. et Biophys. Acta*, **367**, 167 (1974).
5. S. Marcelja, *Nature*, **241**, 451 (1973).
6. M. Luban in "Phase Transition and Critical Phenomena" Vol 5A edited by C. Domb and M.S. Green (Academic Press, N.Y. 1976).
7. R. Blinc in Sauola Internazionale Di Fisica, Varenna Italy Vol 59 (1976), K. A. Muller and A. Rigamantic (Editors).
8. B. Mely, J. Charvolin and P. Keller, *Chem. Phys. Lipids*, **15**, 161 (1975).