Backbone Ordering in Amphiphile Monolayers

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In this paper we describe a lattice density functional theory for the rotator-herringbone phase transition in a liquid supported monolayer system of long chain acids or alcohols. It is assumed that both phases have long-range translational order and that the rotator phase is characterized by a uniform distribution of backbone orientation. We find that orientational interactions among the backbone planes are sufficient to drive a second order transition, and we characterize the phase of the system by a parameter associated with the width of the peaks in a distribution which describes the orientations of the backbones. We also briefly discuss generalizations of the theory to include lattice vibrations and distortions.

I. INTRODUCTION

Recent X-ray diffraction[1] and infrared absorption studies[2] of liquid-supported monolayers of long chain alcohols and acids at high surface pressures have established the existence of a phase transition between a hexatic or hexagonal solid rotator phase and a phase in which the backbone planes defined by the all trans C-C-C bonds of the alkyl chain are locked into preferred orientations. This transition is but one of the many observed in liquid supported monolayers in a small density domain near the close packed density. There has been considerable theoretical effort directed at explaining the rich phase diagram of such systems. Selinger and Nelson[3] applied Landau theory to interpret tilting transitions among hexatic phases of two dimensional liquid crystal systems of rod-like molecules, and have calculated a phase diagram parameterized by elastic constants which appear in their model Hamiltonian. They also exploited renormalization group techniques to go beyond the mean-field calculation of the phase diagram, and have explicitly considered the change in the topology of the phase diagram due to fluctuations. Kaganer and Loginov[4] explained the multitude of high density condensed phases of a Langmuir monolayer of rod-like molecules using a mean-field analysis of a Landau expansion of the free energy which includes an order parameter for collective tilt as well as two additional order parameters which describe one-dimensional weak crystallization of the orientations of the all trans Carbon backbones of the absorbed molecules. The stability criteria for the existence of an n-dimensional crystal require that, by virtue of the assumption of stable embedded weak one dimensional crystallization, the Kaganer-Loginov analysis assumes the monolayer to be three dimensional.

An alternative to the Landau theory of the phase transitions in amphiphile monolayers, namely density functional theory, exploits the functional relationships among the various distribution functions of the system. The advantage of the density functional approach lies in the fact that detailed knowledge of the external, inter and intra-chain potentials is not required as the influence of the potentials is embedded in the singlet distribution function $\rho^{(1)}(\mathbf{x})$. Density functional theory relies on an expansion of the singlet distribution function in a new phase around the form of the singlet distribution function in a reference phase, and is expected to give accurate predictions of the properties of a system near a weak first-order transition. Cai and Rice[5] have successfully applied density functional theory to the tilting transition in long-chain amphiphile monolayers, correctly predicting the direction, magnitude and the dependence on surface area per molecule of the collective tilting in the $S - L_2$ phase transition.

This paper presents a simple lattice density functional theory of the backbone ordering transition. We postulate a model potential for the steric interactions between the backbones of the elliptical cylinder-like molecules in a system where the center of mass of each cylinder is located at a lattice site of a two dimensional hexagonal crystal. For simplicity, we will assume that the intra-chain and interface motions which occur at nonzero temperature allow a psuedo two dimensional hexagonal crystal to have long-ranged order and construct a lattice model for the orientational interactions of the backbones. As in the standard treatment of liquid crystal transitions[6], the order parameter A_s characterizing the phase of the system is related to the average of $\cos^2\theta$ over the effective angular distribution. We find, for the model system described, that as the temperature is decreased there is a second-order transition at $T = T^*$ from the rotator phase ($A_s = 0$) to the herringbone phase ($A_s \neq 0$).

We analyze the self-consistent equations for the order paramaters obtained in the density functional theory when the mean spherical closure approximation (MSA) and a Percus-Yevick-like (PY) closure assumption are used for the direct correlation function. Under the MSA the lattice density functional analysis reduces to a Maier-Saupe-like[6] analysis, while the PY-like assumption predicts a more rapid decrease in the width of the angular distribution function as the temperature is lowered in the vicinity of the transition temperature T^*. The predictions of both mean field theories of the transition are in satisfactory agreement with the limited available experimental data, and it is not possible to determine from the available experimental evidence which closure approximation is more appropriate. Of course, mean field theory will not describe the system behavior in the immediate vicinity of the transition, but there are no experimental data for that region currently available.

II. DENSITY FUNCTIONAL THEORY

A. General Formalism of Density Functional Theory

The basic approach of density functional theory is to treat equilibrium systems as special cases of non-uniform systems[11]. The inhomogeneous equilibrium state for a system in an external potential $U(\mathbf{x}_N)$, where $\mathbf{x}_N$ represents the phase point of an N particle system, is determined variationally from the grand potential $\Omega_V = -pV$. The formulation of density functional theory is based on the idea that the singlet density distribution $\rho^{(1)}(\mathbf{x})$ is a functional of the external potential in a unique way: For a given interaction potential $V(\mathbf{x}_N)$, $\rho^{(1)}(\mathbf{x})$ is uniquely determined by $U(\mathbf{x}_N)$ and vice-versa. This one-to-one correspondence allows the role of the external potential and $\rho^{(1)}(\mathbf{x})$ to be inverted.

The equilibrium density distribution for a general system can be represented in the form

$$\rho^{(1)}(\mathbf{x}_1) = z * \exp\left\{\left(-\beta U(\mathbf{x}_1) + C\left[\rho^{(1)};\mathbf{x}_1\right]\right)\right\}, \tag{2.1}$$

where $C\left[\rho^{(1)}(\mathbf{x}_1)\right]$ is the effective one-body potential energy for non-ideal systems and

$$z = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \exp\left\{\frac{\mu}{k_B T}\right\} \tag{2.2}$$

is the fugacity of the system at temperature T. If we define

$$\phi\left[\rho\right] = k_B T \int d\mathbf{x}\ \rho(\mathbf{x}) \left(\log\left[\left(\frac{h^2}{2\pi m}\right)^{\frac{3}{2}} \rho(\mathbf{x})\right] - 1\right) - \Gamma(\rho), \tag{2.3}$$

where

$$\Gamma(\rho) = \Omega_V\left[\rho\right] + \int d\mathbf{x}\ \rho^{(1)}(\mathbf{x}) u(\mathbf{x}) \tag{2.4}$$

and $u(\mathbf{x}) \equiv \mu - U(\mathbf{x})$, it is straightforward to show that

$$C\left[\rho\right] = \beta \frac{\delta \phi\left[\rho\right]}{\delta \rho(\mathbf{x})}, \tag{2.5}$$

and hence

$$\Omega_V\left[\rho\right] = -\phi\left[\rho\right] + k_B T \int d\mathbf{x}\, \rho(\mathbf{x}) \left(C\left[\rho\right] - 1\right), \tag{2.6}$$

and

$$\left(\frac{\delta \Omega_V\left[\rho\right]}{\delta \rho(\mathbf{x})}\right)_{\rho(\mathbf{x}) = \rho^{(1)}(\mathbf{x})} = 0. \tag{2.7}$$

In a transition between phases A and B the functional form of the equilibrium density distribution changes. At the phase transition point, both the fugacities and the pressures of phases A and B are equal (representing chemical and mechanical equilibrium, respectively), and hence the grand potentials Ω_V are equal. Equation (2.1) is a nonlinear self-consistent equation for the equilibrium density distribution which can be manipulated to obtain

$$\begin{aligned} \rho_a^{(1)}(\mathbf{x}) &= z_a \exp\left\{-\beta U_a(\mathbf{x}) + C\left[\rho_a^{(1)}(\mathbf{x})\right]\right\} \\ &= \rho_b^{(1)}(\mathbf{x}) \exp\left\{\beta\left(\mu_a - \mu_b\right) - \beta\left(U_a(\mathbf{x}) - U_b(\mathbf{x})\right) + \Delta C\left[\rho_a^{(1)}(\mathbf{x}); \rho_b^{(1)}(\mathbf{x})\right]\right\}, \end{aligned} \tag{2.8}$$

where

$$\begin{aligned} \Delta C\left[\rho_a^{(1)}(\mathbf{x}); \rho_b^{(1)}(\mathbf{x})\right] &\equiv C\left[\rho_a^{(1)}(\mathbf{x})\right] - C\left[\rho_b^{(1)}(\mathbf{x})\right] \\ &= \int d\mathbf{x}_2 \; C_2\left[\rho_b^{(1)}; \mathbf{x}, \mathbf{x}_2\right]\left(\rho_a^{(1)}(\mathbf{x}_2) - \rho_b^{(1)}(\mathbf{x}_2)\right) + \ldots \end{aligned} \tag{2.9}$$

and $C_2\left[\rho_b^{(1)}; \mathbf{x}, \mathbf{x}_2\right]$ is the direct correlation function in phase B. Similarly, the free energy difference between the two phases is calculated to be

$$\begin{aligned} \frac{\Delta F}{k_B T} = &- \int d\mathbf{x}_1 \; \left(\rho_a^{(1)}(\mathbf{x}_1) - \rho_b^{(1)}(\mathbf{x}_1)\right) \\ &+ \frac{1}{2}\int d\mathbf{x}_1 d\mathbf{x}_2 \; \left(\rho_a^{(1)}(\mathbf{x}_1) + \rho_b^{(1)}(\mathbf{x}_1)\right) C_2\left[\rho_b^{(1)}; \mathbf{x}_1, \mathbf{x}_2\right]\left(\rho_a^{(1)}(\mathbf{x}_2) - \rho_b^{(1)}(\mathbf{x}_2)\right) + \ldots \end{aligned} \tag{2.10}$$

B. Lattice Density Functional Theory of the Monolayer

The theory we present here resembles the work of Oxtoby and Lipkin on the smectic phase transitions in liquid crystal systems[12], and is intended to capture the qualitative aspects of the orientational ordering transition. We are interested in describing phase transitions in a liquid supported monolayer system of long chain amphiphiles such as $C_{21}H_{43}OH$. We will assume that in the region of the phase diagram of interest, where the system is relatively incompressible, the adsorbed molecule has an all trans conformation and that the system is crystalline (i.e. exhibits long-range spatial order). Computer simulations of amphiphile monolayers have shown that at high surface pressure (π near 30 dynes/cm) and low area per molecule (A near 20 $\mathring{A}^2$/molecule), the molecules in the monolayer are essentially free of gauche conformations (defects)[8]. In this region of the $\pi - A$ isotherm, the x-ray scattering data are consistent with the assumption of true long-range (crystalline) order. Since the backbone plane in each molecule is fairly stiff, we ignore torsions of the bonds and treat every molecule as a rigid body. We then assign an angle θ to its backbone plane, where θ is measured from an arbitrary fixed axis which we set to be along the $\hat{\mathbf{y}}$ direction in the xy plane. Intra-molecular and interfacial motions of the system allow for the possibility of true long-range order since the system is essentially three dimensional. For simplicity, we restrict the centers of mass of the rod-like molecules to the lattice sites of a two dimensional hexagonal crystal and construct a lattice theory for the orientational transition of the backbones.

The backbone planes interfere with one another when the area-per-molecule of the monolayer decreases and steric interactions prevent the backbones from rotating freely. The steric interactions can be minimized in the hexagonal crystal by slightly distorting the crystal along one of the rows of molecules so that two of the six nearest neighbors around each central molecule are separated by a distance slightly larger than the distance to the other four neighbors. The steric interactions are minimized by aligning together the backbones of the molecules along the long axis of the distorted hexagonal cell and fixing the backbones of the four other neighbors perpendicular to the planes along the long axis (see fig. 1). Since these interactions are steric in nature, we expect that next-nearest neighbor interactions are relatively unimportant. Experimentally, very little distortion of the hexagonal crystal is observed, with the long axis being about $6-8$ percent longer than the lattice spacing in the undistorted crystal[1]. In order to capture the qualitative features of the problem, we will assume no distortion of the lattice as the backbone planes order, and neglect any area-per-molecule change across the transition.

The lattice vectors $\mathbf{R}$ for our hexagonal crystal system with a rectangular unit cell (see fig. 1), and a vector $\boldsymbol{\tau}$ are defined by

$$\begin{aligned}\boldsymbol{\tau} &= \frac{1}{2}\left(\mathbf{r}_1 + \mathbf{r}_2\right) \\ \mathbf{R} &= l_1\mathbf{r}_1 + m_1\mathbf{r}_2,\end{aligned} \tag{2.11}$$

where

$$\begin{aligned}\mathbf{r}_1 &= a\hat{\mathbf{x}} \\ \mathbf{r}_2 &= b\hat{\mathbf{y}} = \alpha a\hat{\mathbf{y}}\end{aligned} \tag{2.12}$$

and a is the lattice spacing of the system. In a crystal with hexagonal structure, $\alpha = \sqrt{3}$. Note that from (2.12), in a hexagonal crystal the six nearest neighbors around each molecule are separated by the lattice spacing a since $|\boldsymbol{\tau}| = a$.

We assume that the singlet distribution function for phases A (herringbone phase) and B (rotator phase) are

$$\begin{aligned}\rho_a^{(1)}(\mathbf{r}_1,\theta_1-\chi) &= \sum_{\mathbf{R}_1}\Big[\delta(\mathbf{r}_1-\mathbf{R}_1)f_a(\theta_1-\chi) + \delta(\mathbf{r}_1-\boldsymbol{\tau}-\mathbf{R}_1)g_a(\theta_1-\chi)\Big] \\ \rho_b^{(1)}(\mathbf{r}_1,\theta_1-\chi) &= \frac{1}{2\pi}\sum_{\mathbf{R}_1}\Big[\delta(\mathbf{r}_1-\mathbf{R}_1) + \delta(\mathbf{r}_1-\boldsymbol{\tau}-\mathbf{R}_1)\Big],\end{aligned} \tag{2.13}$$

where $\mathbf{R}_1$ is a lattice vector, $\boldsymbol{\tau}$ is the special vector defined in equation (2.11) and χ is the most probable orientation of the backbone plane with respect to the fixed $\hat{\mathbf{y}}$ axis from which the angle θ_1 is measured. The herringbone phase has the symmetry

$$\rho_a^{(1)}(\mathbf{r}_1, \theta_1) = \rho_a^{(1)}(\mathbf{r}_1 + \boldsymbol{\tau}, \theta_1 \pm \pi/2), \tag{2.14}$$

which implies that

$$f_a(\theta \pm \pi/2) = g_a(\theta). \tag{2.15}$$

For simplicity of presentation, we assume that $f_a(\theta) = f_a(-\theta)$, although a more general class of distribution functions can be considered which leads to the results presented here. We parameterize the orientational distribution function in phases A and B in a general way by expanding the distribution function in terms of normalized Chebyshev polynomials $T_l(x)$,

$$\begin{aligned} f_a(\theta) &= \sum_{l=0}^{\infty} A_l T_l(\cos\theta) \\ g_a(\theta) &= \sum_{l=0}^{\infty} B_l T_l(\cos\theta) \\ f_b(\theta) &= \frac{1}{\sqrt{2\pi}} T_0(\cos\theta), \end{aligned} \tag{2.16}$$

where

$$\begin{aligned} T_0(\cos\theta) &= \frac{1}{\sqrt{2\pi}} \\ T_n(\cos\theta) &= \frac{1}{\sqrt{\pi}} \cos n\theta \end{aligned} \tag{2.17}$$

for n a nonzero positive integer. The Chebyshev functions are orthogonal in the sense that

$$\int_0^{2\pi} d\theta \; T_m(\cos\theta) T_n(\cos\theta) = \delta_{m,n} \ , \tag{2.18}$$

which implies that the coefficients A_n are given by

$$A_n = \int_0^{2\pi} d\theta \; T_n(\cos\theta) f(\theta). \tag{2.19}$$

In addition, we require the symmetry $f(\theta) = f(\theta \pm \pi)$, since the backbone planes are symmetric when rotated by π radians, and hence the odd coefficients A_{2l+1} vanish. We can express the parameters $\mathbf{B}$ in terms of $\mathbf{A}$ by noting that

$$f_a(\theta \pm \pi/2) = g_a(\theta) = \mathbf{A} \cdot \mathbf{T}(\sin\theta), \tag{2.20}$$

and hence

$$B_{2n} = (-1)^n A_{2n}. \tag{2.21}$$

The bulk density $\overline{\rho}$ in both phases is given by

$$\frac{1}{V}\int d\mathbf{r} \int_0^{2\pi} d\theta \; \rho_a^{(1)}(\mathbf{r},\theta) = \frac{2}{A_c} = \frac{1}{V}\int d\mathbf{r} \int_0^{2\pi} d\theta \; \rho_b^{(1)}(\mathbf{r},\theta) = \overline{\rho}, \tag{2.22}$$

where $A_c = \sqrt{3}a^2$ is the area of the unit cell. From equations (2.13) and (2.16) we see that the parameters $\mathbf{A}$ are determined by

$$\frac{1}{2V}\int d\mathbf{r} \int_0^{2\pi} d\theta \; \mathbf{T}(\cos\theta)\left(1+\cos\left(\frac{2\pi\mathbf{r}\cdot\hat{\mathbf{x}}}{a}\right)\right)\frac{\rho_a^{(1)}(\mathbf{r},\theta)}{\overline{\rho}} = \mathbf{A}. \tag{2.23}$$

Utilizing equation (2.8), we finally obtain a self-consistent equation for the order parameters $\mathbf{A}$:

$$\mathbf{A} = \frac{1}{2V}\int d\mathbf{r} \int_0^{2\pi} d\theta \; \mathbf{T}(\cos\theta)\left(1+\cos\left(\frac{2\pi\mathbf{r}\cdot\hat{\mathbf{x}}}{a}\right)\right)\frac{\rho_b^{(1)}(\mathbf{r},\theta)}{\overline{\rho}}\exp\left\{\gamma\left(\mathbf{A},\mathbf{r},\theta\right)\right\} \tag{2.24}$$

where

$$\begin{aligned}\gamma(\mathbf{A},\mathbf{r},\theta) \equiv{}& \beta(\mu_a-\mu_b) - \beta\left(U_a(\mathbf{r},\theta)-U_b(\mathbf{r},\theta)\right) \\ &+ \int d\mathbf{r}' \int_0^{2\pi} d\theta' \; C_2^b\left[\mathbf{r},\mathbf{r}',\theta,\theta'\right]\left(\rho_a^{(1)}(\mathbf{r}',\theta') - \rho_b^{(1)}(\mathbf{r}',\theta')\right) + \ldots.\end{aligned} \tag{2.25}$$

In solving the equations for the order parameters we shall assume that, since the phases have the same translational lattice structure, the external potential due to the interface is the same for both phases, i.e. $U_a(\mathbf{r},\theta) = U_b(\mathbf{r},\theta)$. Furthermore, at chemical equilibrium $\mu_a = \mu_b$, and the self-consistent equation for $\mathbf{A}$ simplifies further.

When the singlet distribution is of the form in equation (2.13) where the molecules are confined to lattice sites, we find the angular distribution function is given by

$$f_a(\theta-\chi) = \frac{\exp\{\gamma(\mathbf{A},\theta-\chi)\}}{N_0(\mathbf{A})}, \tag{2.26}$$

where $N_0(\mathbf{A})$ is a normalization constant given by

$$N_0(\mathbf{A}) = \int_0^{2\pi} d\theta \exp\{\gamma(\mathbf{A},\theta)\}. \tag{2.27}$$

To obtain equation (2.27), we have used the fact that for an arbitrary function $G(\theta)$ with the property $G(\theta\pm2\pi) = G(\theta)$,

$$\int_0^{2\pi} d\theta \; G(\theta-\chi) = \int_0^{2\pi} d\theta \; G(\theta). \tag{2.28}$$

For the lattice model, we find

$$\gamma(\mathbf{A},\theta) = \mathbf{T}(\cos\theta)\cdot\sum_{\mathbf{R}_2}\Big[\mathbf{C}(\mathbf{R}_1,\mathbf{R}_2)\cdot\boldsymbol{\Delta}^-\rho^{(1)}(\mathbf{R}_2) + \mathbf{C}(\mathbf{R}_1,\mathbf{R}_2+\boldsymbol{\tau})\cdot\boldsymbol{\Delta}^-\rho^{(1)}(\mathbf{R}_2+\boldsymbol{\tau})\Big], \tag{2.29}$$

and the free energy difference between the phases is given by

$$\begin{aligned}\frac{\Delta F}{k_B T} = \frac{1}{2}\sum_{\mathbf{R}_1,\mathbf{R}_2} &\Big[\boldsymbol{\Delta}^+\rho^{(1)}(\mathbf{R}_1)\cdot\mathbf{C}(\mathbf{R}_1,\mathbf{R}_2)\cdot\boldsymbol{\Delta}^-\rho^{(1)}(\mathbf{R}_2)+ \\ &+\boldsymbol{\Delta}^+\rho^{(1)}(\mathbf{R}_1+\boldsymbol{\tau})\cdot\mathbf{C}(\mathbf{R}_1+\boldsymbol{\tau},\mathbf{R}_2)\cdot\boldsymbol{\Delta}^-\rho^{(1)}(\mathbf{R}_2)+ \\ &+\boldsymbol{\Delta}^+\rho^{(1)}(\mathbf{R}_1)\cdot\mathbf{C}(\mathbf{R}_1,\mathbf{R}_2+\boldsymbol{\tau})\cdot\boldsymbol{\Delta}^-\rho^{(1)}(\mathbf{R}_2+\boldsymbol{\tau})+ \\ &+\boldsymbol{\Delta}^+\rho^{(1)}(\mathbf{R}_1+\boldsymbol{\tau})\cdot\mathbf{C}(\mathbf{R}_1+\boldsymbol{\tau},\mathbf{R}_2+\boldsymbol{\tau})\cdot\boldsymbol{\Delta}^-\rho^{(1)}(\mathbf{R}_2+\boldsymbol{\tau})\Big],\end{aligned} \tag{2.30}$$

where

$$C_{lm}\left[\mathbf{R}_1,\mathbf{R}_2\right] \equiv \int_0^{2\pi} d\theta_1 d\theta_2\; T_l(\cos\theta_1)T_m(\cos\theta_2)C_2^b\left[\mathbf{R}_1,\mathbf{R}_2,\theta_1+\chi,\theta_2+\chi\right], \tag{2.31}$$

and

$$\left(\Delta^{\pm}\rho^{(1)}(\mathbf{R}_1)\right)_l = A_l \pm \frac{1}{\sqrt{2\pi}}\delta_{l,0} \tag{2.32}$$

$$\left(\Delta^{\pm}\rho^{(1)}(\mathbf{R}_1+\boldsymbol{\tau})\right)_l = B_l \pm \frac{1}{\sqrt{2\pi}}\delta_{l,0}. \tag{2.33}$$

From equations (2.32), (2.33), (2.29) and (2.24), we get a system of self-consistent equations for the order parameters A_{2n};

$$A_{2n} = \int_0^{2\pi} d\theta\; \frac{T_{2n}(\cos\theta)}{N_0(\mathbf{A})}\exp\{\gamma(\mathbf{A},\theta)\}. \tag{2.34}$$

It should be noted that $\Delta^-\rho^{(1)} = 0$ in equation (2.34) guarantees that $A_l = A_0\delta_{l,0} \equiv X_l$, so equation (2.34) always has the trivial solution $\mathbf{A} = \mathbf{X}$, which corresponds to the rotator phase. The goal is to search for a nontrivial solution $\mathbf{A} \neq \mathbf{X}$.

The only remaining aspect of the theory to be described is the calculation of the direct correlation function in the reference phase B. In general, this is done via the Ornstein-Zernike relation

$$\begin{aligned}h(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2) &= c(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2) \\ &+\int d\mathbf{r}_3\int_0^{2\pi} d\theta_3\; c(\mathbf{r}_1,\mathbf{r}_3,\theta_1,\theta_3)\rho_b^{(1)}(\mathbf{r}_3,\theta_3)h(\mathbf{r}_3,\mathbf{r}_2,\theta_3,\theta_2),\end{aligned} \tag{2.35}$$

where $h(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2)$ is defined to be

$$h(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2) = \frac{\rho_b^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2)}{\rho_b^{(1)}(\mathbf{r}_1,\theta_1)\rho_b^{(1)}(\mathbf{r}_2,\theta_2)} - 1, \tag{2.36}$$

and $\rho_b^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \theta_1, \theta_2)$ is the pair distribution function for the system in phase B. Since the h function exists only at special spatial positions, the Ornstein-Zernike equation (OZ) can be written

$$\mathbf{h}(\mathbf{R}_1, \mathbf{R}_2) = \mathbf{C}(\mathbf{R}_1, \mathbf{R}_2) + \frac{1}{2\pi} \sum_{\mathbf{R}_3} \left[\mathbf{C}(\mathbf{R}_1, \mathbf{R}_3) \cdot \mathbf{h}(\mathbf{R}_3, \mathbf{R}_2) + \mathbf{C}(\mathbf{R}_1, \mathbf{R}_3 + \boldsymbol{\tau}) \cdot \mathbf{h}(\mathbf{R}_3 + \boldsymbol{\tau}, \mathbf{R}_2) \right], \tag{2.37}$$

where $\mathbf{C}(\mathbf{R}_1, \mathbf{R}_2)$ is defined by equation (2.31), and

$$h_{lm}(\mathbf{R}_1, \mathbf{R}_2) = \int_0^{2\pi} d\theta_1 d\theta_2 \; T_l(\cos\theta_1) T_m(\cos\theta_2) h(\mathbf{R}_1, \mathbf{R}_2, \theta_1 + \chi, \theta_2 + \chi). \tag{2.38}$$

In equation (2.37), the dot notation means a sum over repeated labels for the coefficients in the Chebyshev series expansion. To solve equation (2.37), the Chebyshev series expansion must be truncated so that all the $\mathbf{h}$ and $\mathbf{C}$ are finite-rank square matrices. Inverting the OZ equation to solve for the $\mathbf{C}$ matrix involves inverting an $N \times M$ dimensional square matrix, where N is the number of Chebyshev terms in the series expansions of the orientational distribution function and M is the number of lattice points retained in the sum over lattice sites. We generally expect that $\mathbf{C}(\mathbf{R}_1, \mathbf{R}_2)$ is a short-ranged function of the relative arguments $\mathbf{R}_1 - \mathbf{R}_2$, and hence M should be fairly small. Clearly, as the number of lattice sites retained increases, the matrix operations become more cumbersome to carry out.

C. Mean-Spherical Closure Assumption

We evaluate the density functional theory using two simple closure assumptions for the Ornstein-Zernike equation. We assume that the site-site interaction potential V can be written in terms of an isotropic part V_0 and an anisotropic part V_a,

$$V(\mathbf{r}_1, \mathbf{r}_2, \theta_1, \theta_2) = V_0(\mathbf{r}_1, \mathbf{r}_2) + V_a(\mathbf{r}_1, \mathbf{r}_2, \theta_1, \theta_2), \tag{2.39}$$

where

$$\begin{gathered} V_a(\mathbf{r}_1, \mathbf{r}_2, \theta_1, \theta_2) = -V \times \\ \left({\sum_{\mathbf{R}_1, \mathbf{R}_2 \neq \mathbf{R}_1}}' \Big(\delta(\mathbf{r}_1 - \mathbf{R}_1)\delta(\mathbf{r}_2 - \mathbf{R}_2) + \delta(\mathbf{r}_1 + \boldsymbol{\tau} - \mathbf{R}_1)\delta(\mathbf{r}_2 + \boldsymbol{\tau} - \mathbf{R}_2) \Big) \frac{(2\cos^2\theta_{12} - 1)}{2} \right. \\ \left. + {\sum_{\mathbf{R}_1, \mathbf{R}_2}}' \Big(\delta(\mathbf{r}_1 - \boldsymbol{\tau} - \mathbf{R}_1)\delta(\mathbf{r}_2 - \mathbf{R}_2) + \delta(\mathbf{r}_1 - \mathbf{R}_1)\delta(\mathbf{r}_2 + \boldsymbol{\tau} - \mathbf{R}_2) \Big) \frac{(2\sin^2\theta_{12} - 1)}{4} \right), \end{gathered} \tag{2.40}$$

where $\theta_{12} = \theta_1 + \theta_2$ and θ_1 is the backbone angle for the molecule at spatial position $\mathbf{r}_1$. In equation (2.40), the prime on the sums indicates that only the six nearest neighbors interact with a given molecule. The difference in the barrier heights for molecules separated by a lattice vector and molecules separated by the vector $\boldsymbol{\tau}$ is consistent with the overall symmetry properties of the herringbone phase so that in the mean-spherical approximation, $\gamma(\mathbf{A},\mathbf{R},\theta) = \gamma(\mathbf{A},\mathbf{R}+\boldsymbol{\tau},\theta-\pi/2)$. Other potentials, such as the quadrupole-quadupole potential in the planar-rotor model[22] give equivalent results in the MSA. It should be emphasized that the potential postulated here is designed to mimic steric interactions of the backbone planes of elliptical molecules in a closely packed crystal and does not include an anisotropic Van-der-Waals attractive potential which was originally thought to be responsible for the alignment of rod-like molecules in nematic liquid crystals[6,7]. Currently, it is believed that the anisotropic part of the attractive potential is relatively unimportant in the description of the nematic phase transition, and that the Onsager excluded volume effects (covolume) dominate the effective potential[9,10]. The potential presented here is intended to qualitatively account for the hard-core ellipsoid repulsive interactions in a system with relatively weak long-range Van-der-Waals interactions.

We break up the direct correlation function for the system into an isotropic part $C_0(\mathbf{r}_1,\mathbf{r}_2)$ and an anisotropic part $C_a(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2)$ and use the so called "mean-spherical" closure approximation (MSA) for the direct correlation function in the high temperature rotator phase:

$$\begin{aligned} C_a(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2) &= \frac{-g_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2)}{k_BT} V_a(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2) \qquad \text{for } |\mathbf{r}_1-\mathbf{r}_2| \geq a \\ g^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2) &= 0 \qquad \text{for } |\mathbf{r}_1-\mathbf{r}_2| < a \ , \end{aligned} \tag{2.41}$$

where a is the lattice spacing,

$$\begin{aligned} g_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\rho_0^{(1)}(\mathbf{r}_1)\rho_0^{(1)}(\mathbf{r}_2) &= \rho_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \\ g^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2)\rho^{(1)}(\mathbf{r}_1,\theta_1)\rho(1)(\mathbf{r}_2,\theta_2) &= \rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2) \end{aligned} \tag{2.42}$$

and $\rho_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ is the pair-correlation function for a system with the isotropic interaction potential V_0. Since the anisotropic interaction potential V_a is due to steric repulsions, we will assume that as $|\mathbf{r}_1-\mathbf{r}_2|$ vanishes $C(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2)$ approaches the isotropic direct correlation $C_0(\mathbf{r}_1,\mathbf{r}_2)$. Equation (2.41) has been shown to be a good closure approximation for the evaluation of the pair-correlation function at high temperatures for a system of linear molecules[13], and has been tested recently and proven to be a good approximation for a solvable lattice gas model.[14] It should be noted that the generalized mean field closure approximation used by Henderson and Gray[13] in which

$$\begin{aligned} C_a(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2) = &\frac{-g_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2)}{k_BT} V_a(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2) \\ &+ \left(g_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2)-1\right)\left(h_a(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2) - C(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2)\right) \end{aligned} \tag{2.43}$$

also reduces to the MSA for the lattice system where $g_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = 1$.

Given the form of the anisotropic potential, in the MSA we find that

$$\gamma(\mathbf{A},\mathbf{R},\theta) = 2W\pi A_2 \cos 4\chi\, T_2(\cos\theta) = 2W\sqrt{\pi}A_2 \cos 4\chi\, \cos 2\theta$$
$$= 2WA_s \cos 4\chi\, \cos 2\theta, \tag{2.44}$$

where $A_s = \sqrt{\pi}A_2$ and $W = V/k_BT$, and hence the self-consistent system of equations for the order parameter is

$$A_{2n} = \int_0^{2\pi} d\theta\, \frac{T_{2n}(\cos\theta)}{2\pi I_0(2WA_s\cos 4\chi)} \exp\{2WA_s \cos 4\chi\, \cos 2\theta\}, \tag{2.45}$$

or

$$A_s = \frac{I_1(2WA_s\cos 4\chi)}{I_0(2WA_s\cos 4\chi)}, \tag{2.46}$$

where $I_n(x)$ is the nth order modified Bessel function. Equation (2.46) has a non-zero solution when $W/\cos 4\chi > 1$, as can be seen graphically by plotting the function $I_1(2x)/I_0(2x)$. From equation (2.30), the excess free energy and entropy differences between phases A and B are

$$f^\chi = \frac{F^\chi}{Nk_BT} = 2WA_s^2\cos 4\chi - 2\log\left(2\pi I_0(2WA_s\cos 4\chi)\right)$$
$$\frac{S^\chi}{Nk_B} = 2\log\left(2\pi I_0(2WA_s\cos 4\chi)\right) - 4WA_s^2\cos 4\chi. \tag{2.47}$$

The most probable orientation of the backbone planes and the value of the order parameter A_s are found by minimizing the excess free energy with respect to A_s and χ. We find that the conditions

$$\frac{\partial f^\chi}{\partial \chi} = 0 = \frac{\partial f^\chi}{\partial A_s} \tag{2.48}$$

imply A_s obeys the self-consistent equation (2.46) and that the most probable orientation of the backbones is $\chi = n\pi/4$. The values of A_s and χ obtained from (2.48) minimize the excess free energy at nonzero A_s when

$$1 - W\cos 4\chi + W\cos 4\chi A_s^2 > 0. \tag{2.49}$$

Numerically, we find that this condition holds for

$$\begin{aligned} \chi &= \frac{n\pi}{2} &\quad \text{when} \quad & W > 1 \\ \chi &= \frac{(2n+1)\pi}{4} &\quad \text{when} \quad & W < -1. \end{aligned} \tag{2.50}$$

This identifies the transition temperature as $T^* = \cos 4\chi\, V/k_B$. The constant volume heat capacity C_v is given by

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_v = -4Nk_BA_s\left(\frac{\partial A_s}{\partial T}\right)_v$$
$$= \frac{-2Nk_BA_s^2}{T}\frac{\left(T - 2T^*(1-A_s^2)\right)}{\left(T - T^*(1-A_s^2)\right)}. \tag{2.51}$$

Numerically, we find C_v is discontinuous at the transition temperature;

$$C_v = \begin{cases} 4Nk_B & \text{for} \quad T < T^* \\ 0 & \text{for} \quad T \geq T^*, \end{cases} \tag{2.52}$$

which in turn implies that the order parameter A_s goes to zero as T approaches the transition temperature as $(T - T^*)^\beta$, with $\beta = 1/2$. These critical exponents agree with the critical exponents predicted by a mean field analysis of a Landau-Ginzburg Hamiltonian.

D. Numerical Results

The self-consistent equation (2.46) for the order parameter A_s must be solved numerically by iteration. We have solved for A_s using Gaussian quadrature integration techniques and have obtained the order parameter with an accuracy of one part per million. For $V > 0$ and $\chi = n\pi/2$, we find a second order transition ($\Delta S = 0$) at an effective temperature of $T^* = V/k_B$. In figure 2 we show the calculated value of the order parameter A_s as a function of the reduced temperature T/T^* and we clearly see that as T approaches the transition temperature T^* the order parameter drops continuously to zero, its value in the rotator phase. In figure 3, we show the free energy versus reduced temperature. In figure 4 we show the orientational distribution function at various reduced temperatures and, finally, in figure 5 we show the free energy difference isotherms versus the order parameter to demonstrate that the self-consistent solution corresponds to the minimum of the free energy.

E. Percus-Yevick-like Closure

It is possible that other closure approximations will lead to improvements in the theory from both qualitative and quantitative points of view. As an example, we consider another approximation for the anisotropic part of the direct correlation function and examine the consequences for a system with a hard-core potential with an anisotropic tail

$$U(1,2) = \begin{cases} \infty & |\mathbf{r}_1 - \mathbf{r}_2| < a \\ V_1(1,2) & |\mathbf{r}_1 - \mathbf{r}_2| \geq a, \end{cases} \tag{2.53}$$

with

$$\begin{aligned} V_1(1,2) = &- \sum_{\mathbf{R}_1 \neq \mathbf{R}_2}{}' \Big(\delta(\mathbf{r}_1 - \mathbf{R}_1)\delta(\mathbf{r}_2 - \mathbf{R}_2) + \delta(\mathbf{r}_1 - \boldsymbol{\tau} - \mathbf{R}_1)\delta(\mathbf{r}_2 - \boldsymbol{\tau} - \mathbf{R}_2) \Big) \times \\ & \big(V(2\cos^2\theta_{12} - 1) - k_B T \log 2 \big) \\ &- \sum_{\mathbf{R}_1 \neq \mathbf{R}_2}{}' \Big(\delta(\mathbf{r}_1 - \boldsymbol{\tau} - \mathbf{R}_1)\delta(\mathbf{r}_2 - \mathbf{R}_2) + \delta(\mathbf{r}_1 - \mathbf{R}_1)\delta(\mathbf{r}_2 - \boldsymbol{\tau} - \mathbf{R}_2) \Big) \times \\ & \big(V(2\sin^2\theta_{12} - 1) - k_B T \log 4 \big) \, . \end{aligned} \tag{2.54}$$

Once again, the two body potential is constructed in such a way that the predicted singlet distribution function which results by incorporating the closure assumption into the formalism has the correct symmetry properties. We approximate the direct correlation function by

$$C(1,2) = \Big(1 + f_d(1,2)\Big)\exp\{-\beta V_1(1,2)\} - 1 + f_d(1,2)\big(h(1,2) - C(1,2)\big), \tag{2.55}$$

where $f_2(1,2)$ is the Mayer function for a hard core potential

$$f_d(1,2) = \begin{cases} -1 & |\mathbf{r}_1 - \mathbf{r}_2| < a \\ 0 & |\mathbf{r}_1 - \mathbf{r}_2| \geq a. \end{cases} \tag{2.56}$$

Equation (2.55) resembles the Percus-Yevick (PY) equation[15,16]

$$C(1,2) = f(1,2) + f(1,2)\big(h(1,2) - C(1,2)\big) \tag{2.57}$$

with the second full Mayer function $f(1,2) \equiv \exp\{-\beta U(1,2)\} - 1$ on the right hand side of (2.57) replaced by the hard-core Mayer function $f_d(1,2)$. Equation (2.55) is equivalent to setting

$$\begin{aligned} &C(1,2) = \exp\{-\beta V_1(1,2)\} - 1 \qquad && |\mathbf{r}_1 - \mathbf{r}_2| \geq a \\ &g(1,2) = 0 && |\mathbf{r}_1 - \mathbf{r}_2| < a, \end{aligned} \tag{2.58}$$

so we see that the MSA of equation (2.41) corresponds to linearizing (2.58) with respect to $W = V/k_BT$. It should be noted that equation (2.58) implies that the expansion of $C(1,2)$ in terms of Chebyshev polynomials involves terms beyond the second polynomial T_2, unlike the expansion of $C(1,2)$ in the MSA. In general, the magnitude of the coefficients for the higher order terms decreases rapidly with order so that only a few additional polynomial terms must be kept for numerical accuracy in the region of the phase transition. In fact, near the transition at $T = .990T^*$, we find that $\mathbf{A}_{14}/\mathbf{A}_0 \approx 1 \times 10^{-6}$. From (2.54) we find that in the PY-like approximation scheme

$$C_{2l2m}(\mathbf{R}_1, \mathbf{R}_2) = \delta_{l,m} C_{2l2l} = 2(-1)^m C_{2l2m}(\mathbf{R}_1, \mathbf{R}_2 + \boldsymbol{\tau}), \tag{2.59}$$

where

$$C_{2l2l} = \int_0^{2\pi} d\theta_1 d\theta_2\ T_{2l}(\cos\theta_1) T_{2l}(\cos\theta_2) \left(\frac{1}{2}\exp\{W\cos 2(\theta_{12} + 2\chi)\} - 1\right) \tag{2.60}$$

with $\theta_{12} = \theta_1 + \theta_2$, which yields

$$\gamma(\mathbf{A}, \mathbf{R}, \theta) = 4\sum_{n=1}^{\infty} T_{2n}(\cos\theta) C_{2n2n} A_{2n}. \tag{2.61}$$

Utilizing equation (2.34), we obtain the self-consistent solution for the order parameters A_{2n} and find a second order transition at $T^* = 1.105773 V/k_B \cos 4\chi$. Examining the excess free energy of the lattice system, we once again find that the free energy is minimized below the transition temperature by

$$\begin{aligned} \chi &= \frac{n\pi}{2} \qquad \text{when} \qquad W > 1 \\ \chi &= \frac{(2n+1)\pi}{4} \qquad \text{when} \qquad W < -1. \end{aligned} \tag{2.62}$$

We also find that if $\{A'_{2n}\}$ is a solution of (2.34), then $\{(-1)^n A'_{2n}\}$ is as well, which reflects the fact that only the relative orientation of the backbone planes is physically significant. In this PY-like closure scheme, the predicted form of the angular distribution function is not quite Gaussian in $\cos\theta$, and the width of the distribution is a more sensitive function of the reduced temperature T/T^* (see Fig. 6).

Using the Ornstein-Zernike equation, the full PY approximation scheme or any other closure assumption can be implemented, but it is difficult to determine which closure scheme is the most appropriate for the system without directly comparing the predicted heat capacity and width of the angular distribution function for each model at various reduced temperatures to reliable experimental data. Unfortunately, such detailed information is not available at present due to the difficulty of carrying out very accurate x-ray diffraction measurements of the monolayer system.

III. DISCUSSION AND CONCLUSIONS

We have presented a lattice mean field theory for the backbone ordering transition observed in monolayers of long-chain amphiphilic molecules. Our analysis is based upon a model two-body potential designed to account for the effective hard-core repulsive and Van-der-Waals attractive interactions among the backbones of the molecules. An essential feature of the model potential is that the interactions among molecules within a hexagonal (or distorted hexagonal) unit cell are anisotropic;i.e. two of the six nearest neighbors interact differently with the central molecule than the other four. Without this feature, no transition would exist. For $V > 0$, where V is a physical parameter which characterizes the barrier height to rotation of the backbone planes of the crystal, both lattice models predict a second order transition at transition temperature T^*, with $T^* = V/k_B$ and $T^* = 1.105773 V/k_B$ for the MSA and PY system of equations, respectively. From the mean field theories we predict the width and functional form of the orientational distribution functions as a function of reduced temperature T/T^*. The fact that the predicted transition is second order rather than weakly first order may be an artifact of our rigid lattice model. For a system in which no vacancies at sites or change in volume are allowed, the Clapeyron equation of equilibrium thermodynamics demands that $\Delta S = 0$ at the transition or else the thermodynamic derivative $\left(\frac{\partial P}{\partial T}\right) \approx \Delta S/\Delta V$ diverges.

Density functional theory coupled with the MSA is equivalent to a mean field theory adapted from Maier and Saupe's work on the nematic phase transition in liquid crystal systems[6]. In their analysis, the average potential $V_1(\mathbf{r}_1,\theta_1)$ felt by a molecule in a field of others interacting by the pair potential V_{12} is calculated self-consistently via

$$V_1(\mathbf{r}_1,\theta_1) = \int d\mathbf{r}_2 \int_0^{2\pi} d\theta_2 \; \rho^{(1)}(\mathbf{r}_2,\theta_2) V_{12}(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2). \tag{3.1}$$

Using the form of the singlet distribution function and the pair potential in equation (2.40), we obtain the self-consistent equation

$$\alpha = 2W \frac{I_1(\alpha)}{I_0(\alpha)}, \tag{3.2}$$

with $\alpha = 2W\sqrt{\pi}A_2$, which is exactly the result obtained in equation (2.46). This equivalence is not surprising since the effective one body potential in truncated density functional theory is given by

$$C^{(1)}(\mathbf{r}_1,\theta_1) = \int d\mathbf{r}_2 \int_0^{2\pi} d\theta_2 \; C(\mathbf{r}_1,\mathbf{r}_2,\theta_1,\theta_2) \left(\rho_a^{(1)}(\mathbf{r}_2,\theta_2) - \rho_b^{(1)}(\mathbf{r}_2,\theta_2)\right), \tag{3.3}$$

which yields $-\beta V_1(\mathbf{r}_1,\theta_1) = C^{(1)}(\mathbf{r}_1,\theta_1)$ in the MSA.

The planar-rotor model often used to investigate the herringbone orientational transition in monolayer systems of atoms adsorbed on solids[22,23] postulates a quadrupole-quadrupole interaction potential of the form

$$V = K \sum_{\langle ij \rangle} \cos\bigl(2(\theta_i + \theta_j) - 4\phi_{ij}\bigr), \tag{3.4}$$

where θ_i and θ_j are the backbone orientations of molecules located at sites i and j respectively, ϕ_{ij} is the angle between a fixed axis and the vector connecting sites i and j, K is a physical parameter associated with the barrier to free rotation and $\langle ij \rangle$ denotes pairs of nearest neighbor lattice sites. In the MSA, this potential also gives equation (2.45) provided we set $-2K = V$. For $V < 0$, which corresponds to $K > 0$, the most probable orientation of the system is $\chi = \pi/4$ and the transition temperature is $T^* = 2K/k_B$, which are the results of Chacón and Tarazona[22]. In the PY-like approximation scheme we find that the planar-rotor model potential does not give the correct symmetry properties for the singlet distribution function and thus no direct comparison can be made with the results of our model.

The mean-field theory resulting from the PY-like approximation has some similarities with Onsager's work on a dilute system of orientable hard rods[17]. Onsager considered a collection of orientable rods of length L and diameter D interacting through some potential $V(\mathbf{r}_{12},\Omega_1,\Omega_2)$ which depends on both the positions $\mathbf{r}$ and orientations Ω of the rods. The Helmholtz free energy per particle for a system with density ρ was then found to be

$$\frac{F}{Nk_BT} = \log \rho + \int d\Omega_1\, f(\Omega_1) \left(\log f(\Omega_1) + \frac{\rho}{2} \int d\Omega_2 B(\Omega_1, \Omega_2) f(\Omega_2) \right)$$
$$+ \frac{\rho^2}{3} \int d\Omega_1 d\Omega_2 d\Omega_3 f(\Omega_1) f(\Omega_2) f(\Omega_3) C(\Omega_1, \Omega_2, \Omega_3) + \ldots \tag{3.5}$$

The 'virial' coefficients $B(\Omega_1, \Omega_2)$ and $C(\Omega_1, \Omega_2, \Omega_3)$ were found to be, via Mayer cluster theory,

$$B(\Omega_1, \Omega_2) = -\int d\mathbf{r}_2\ f_m(\mathbf{r}_{12}, \Omega_1, \Omega_2)$$
$$C(\Omega_1, \Omega_2, \Omega_3) = -\int d\mathbf{r}_1 d\mathbf{r}_2\ f_m(\mathbf{r}_{12}, \Omega_1, \Omega_2) f_m(\mathbf{r}_{13}, \Omega_1, \Omega_3) f_m(\mathbf{r}_{23}, \Omega_2, \Omega_3),$$

where

$$f_m(\mathbf{r}_{12}, \Omega_1, \Omega_2) = \exp\{-\beta V(\mathbf{r}_{12}, \Omega_1, \Omega_2\} - 1. \tag{3.6}$$

Onsager neglected third and higher 'virial' terms, which was shown to be accurate for $L > 10D^{18}$ near the transition, and assumed hard-wall interactions among the rods and found a first-order nematic transition. The equilibrium form of the distribution function $f(\Omega)$ can be determined variationally by minimizing the free energy subject to the normalization condition, which yields the self-consistent equation

$$f(\Omega_1) = C \exp\left\{ -\rho \int d\Omega_2\ f(\Omega_2) B(\Omega_1, \Omega_2) \right\}, \tag{3.7}$$

where C is a constant determined by normalization. Noting that the singlet distribution function for a dilute gas system of hard rods is $\rho^{(1)}(\mathbf{r}_1, \Omega_1) = \rho f(\Omega_1)$, we see that the Onsager theory corresponds to setting

$$C^{(1)}(\mathbf{r}_1, \Omega_1) = \int d\mathbf{r}_2 \int d\Omega_2\ \rho^{(1)}(\mathbf{r}_2, \Omega_2) f_m(r_{12}, \Omega_1, \Omega_2), \tag{3.8}$$

which is essentially the effective mean field potential obtained in the truncated density functional theory when the PY-like approximation is used for the direct correlation function.

No explicit reference was made in our lattice theory to the actual lattice structure of the crystal other than the assumption that each molecule is surrounded by a first shell of six other "nearest" neighbors. Thus the theory is valid for either hexagonal or slightly distorted hexagonal crystal structures provided the structure remains unchanged during the phase transition. Since a two-dimensional hexatic phase exhibits long range bond orientational order and spatial correlations extend over many molecules, we expect the lattice theory to capture the qualitative aspects of the backbone ordering transion even if the rotator phase does not have long range translational order. One of the appealing aspects of this density functional theory formalism is that it is relatively straightforward to generalize to include lattice vibrations and to allow orthorhombic distortions of the hexagonal lattice as well as density changes.

If the molecules vibrate harmonically around their lattice sites, the delta function distributions like $\delta(\mathbf{r}-\mathbf{R})$ that appear in the model should broaden into Gaussians with a width inversely proportional to the Debye-Waller factor. Furthermore, the pair distribution function can be calculated analytically for the isotropic harmonic potential and the mean spherical approximation or some other closure assumption can be used to complete the analysis and establish self-consistent equations for the order parameters. It is probable that the inclusion of lattice vibrations and distortions will change the predicted ordering transition from second order to the experimentally inferred weakly first order.

X-ray diffraction studies of monolayer systems suggest that the backbone ordering transition is accompanied by a deformation of the hexagonal lattice to a distorted hexagonal lattice structure[19]. In fact, the lattice deformation, which is measured by the ratio $\alpha = b/a$ of the length of the sides b and a of the rectangular two-molecule unit-cell (see figure 1.), is considered to be the indication of the ordering transition. When $\alpha = \sqrt{3}$ (hexagonal structure), the system is assumed to be in a "rotator-II" phase in which the chains which form the backbones of the molecules rotate about the chain axis. As the temperature is lowered at constant pressure, α drops from the value in the hexagonal phase to a value of about $\alpha = 1.5$. There is experimental evidence[19] that an intermediate phase exists between the herringbone phase and the "rotator-II" phase at α values near 1.65. This "rotator-I" phase is characterized by some lattice distortion and partial backbone ordering. The temperature dependence of α and the area-per-molecule in the monolayer system corresponds closely with that observed in thin three-dimensional paraffin systems[20] in which the intermediate "rotator-I" phase is evident. Although our theory is too simple to allow partial ordering of the backbone planes, Kaganer and Loginov[4] have recently constructed a Landau theory which predicts a two-step weak crystallization process for the herringbone transition and which qualitatively agrees with the X-ray diffraction data. A more complete density functional theory should address the questions of how orientational order is coupled to lattice distortions and whether an intermediate rotator phase is present in the monolayer system.

Near the transition temperature, orientational correlations become important and mean field theory breaks down. We have examined the PY-like closure scheme because it is a simple way of incorporating orientational correlations. Another possible way to include correlations and go beyond mean field theory for a rigid lattice system consists of applying cluster variational methods[21]. This technique has been applied[22] to a monolayer system of N_2 molecules adsorbed on graphite interacting via a quadrupole-quadrupole potential for which there are computer simulations[23]. It was found that inclusion of some orientational correlation appreciatively improved the agreement between theory and computer simulation. Since we have no such data with which to compare our theory, it is not possible to determine whether the PY-like closure assumption improves the MSA results or not. However, since the physical system is three dimensional in nature, the fluctuations are not strong enough to destroy the long range order present in the herringbone phase and the overall topology of the phase diagram predicted by both mean field theories should remain intact. Away from the transition temperature the predictions of mean field theory should be satisfactory.

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Figure Captions

Figure 1: Schematic showing the herringbone phase (phase A) and the rotator phase (phase B) with a choice of rectangular unit cell. Note there are two molecules per unit cell. The ellipses in phase A are intended to indicate the preferred orientations of the backbone planes for $V > 0$, whereas the circles in phase B show that there are no preferred orientations in the rotator phase. There is another type of herringbone phase for $V < 0$ in which all the distribution functions have maxima at $\pi/4$ or $3\pi/4$. α is a parameter which describes the lattice structure: $\alpha = \sqrt{3}$ corresponds to a triangular lattice and other values of α indicate a distorted hexagonal structure.

Figure 2: A plot of the order parameter A_s for the MSA model versus the reduced temperature T/T^*. The plot clearly shows the continuous drop in the value of A_s as T approaches T^*. Near the transition temperature, A_s scales as $\sqrt{T - T^*}$.

Figure 3: A plot of the relative excess free energy difference between the herringbone and rotator phases (divided by Nk_BT) versus reduced temperature T/T^*.

Figure 4: A plot of the normalized backbone orientational distribution function for $V > 0$ in the MSA versus θ/π. As the reduced temperature decreases, the distribution function narrows and becomes more peaked around $\pi/2$, the preferred orientation.

Figure 5: A plot of the relative excess free energy difference isotherms versus the order parameter A_s. The value of the order parameter minimizes the excess free energy. For $T = .950T^*$, $A_s = \pm.311$ whereas for $T = .975T^*$, $A_s = \pm.222$, which correspond to the minima of the respective isotherms.

Figure 6: A comparison of the normalized backbone orientational distribution function in the MSA and PY-like approximation schemes. In the PY-like approximation scheme, the width of the peak in the distribution function changes more rapidly and there are slight deviations in functional form from a Gaussian in $\cos 2\theta$.