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# Phase Transitions in Quasi-Two-Dimensional Molecular Solids: Tilt-Induced Elastic Multipoles and Their Interaction and Ferroelasticity in Langmuir Monolayers

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Using a solid state approach, elastic multipoles are demonstrated to be effective for modeling the tilting of molecules in Langmuir monolayers. As shown in a previous paper (Luty, T.; Eckhardt, C. J. *J. Phys. Chem.* **1995**, *99*, 8872), the effective rotational couplings between the molecules are determined by indirect interaction mediated by the elasticity of the medium supplemented by direct coupling. A detailed analysis of this indirect interaction and the idea of using local elastic multipoles to describe fluctuations in orientational degrees of freedom is the thrust of this work. Expressed in terms of spherical harmonics, elastic multipoles provide a convenient and powerful representation of the local stresses and of their interaction as mediated by the elastic field of the monolayer. It is shown that a strong interaction of the elastic dipoles leads to molecular orientational ordering wherein the ordered phase may be characterized as ferroelastic. In particular, it is concluded that monolayer phases with tilts toward nearest neighbor and next nearest neighbor are ferroelastic with the "swiveling" transition between them occurring as a strain reversal process that passes through an undeformed hexagonal lattice of vertical molecules.

## 1. Introduction

Langmuir monolayers are often modeled upon liquid crystals with emphasis on their similarity to liquid rather than crystalline properties. This is quite understandable, since the richness of smectic liquid-crystalline phases compares to the variety of phases observed in Langmuir monolayers.[1] Following the analogy, it has been suggested that mesophases of Langmuir monolayers are hexatic phases.[1−4] Hexatics are, in essence, characterized by short-range, exponentially decaying, translational order but quasi-long-range, algebraically decaying order in the orientations of the "bonds" between the positions of neighboring molecules.[2] The hexatic phase is posited to appear when a two-dimensional (2-D) crystal becomes destabilized by interacting dislocations which preserve the quasi-long-range order of the "bond" orientations. In the process of 2-D melting, the intermediate hexatic phase may be viewed as a 2-D crystal with a frozen pattern of unbound dislocations.[2,3]

It has been recognized that the molecular tilt degree-of-freedom further distinguishes tilted and untilted phases.[5,6] The physics behind this involves elasticity or, more precisely, the coupling between the tilt and macroscopic shear strain. The molecular tilt degree-of-freedom has been represented by the azimuthal angle, $\phi$, and the magnitude of the tilt, $\theta$, has usually been neglected. For definition of these angles see Figure 1. The shear strain has been measured by the bond-order angle, $\vartheta$. Due to tilt−strain coupling, four phases have been identified among hexatics: (i) a phase with no tilt (called unlocked), (ii) a smectic phase I with tilt toward nearest neighbors (NN), (iii) a smectic phase F with tilt toward next nearest neighbors (NNN), and (iv) a smectic phase L with tilt direction intermediate between NN and NNN.

There are doubts, however, that Langmuir monolayer mesophases can be rigorously treated as hexatics. In fact, the hexatic order in Langmuir monolayer mesophases has not been *directly* observed. Grazing incidence X-ray diffraction experiments[7] have shown the monolayers to be crystalline in both
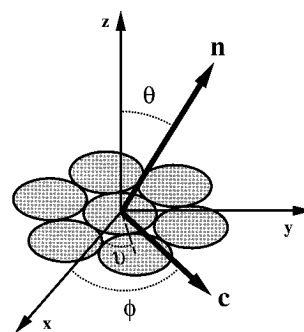


**Figure 1.** Drawing of axes, angles, and directors used in the description of the orientation of a rigid rod model for molecules. *x*, *y*, and *z* define the Cartesian coordinate system with polar angles $\theta$ and $\phi$. $\vartheta$ is the angle formed by a crystallographic hexagonal "bond" axis with the *x*-axis.

compressed and uncompressed states. These crystalline films, essentially quasi-two-dimensional "powders", are weak X-ray scatterers, and distinction between the "powder" and mesophases is neither easy nor definite. As noted by Petersen,[8] the mosaic structure of highly-ordered mesophases is essentially indistinguishable from a polycrystalline texture, and this is the one that occurs commonly in alkanes. So, from an experimental point of view, the hexatic order in mesophases of Langmuir monolayers has not been directly observed. Instead, as pointed out by Kaganer[9] in reference to the X-ray studies, the single peak of the "powder" sample has been *interpreted* as the triply degenerate peak of a hexatic.

Furthermore, from a fundamental point of view, the intrinsic head-tail asymmetry of Langmuir monolayer molecules makes the system quasi-two-dimensional rather than strictly 2-D, for which the hexatics were defined. This is reflected by the fact that the ordering of head groups on the water surface differs from that of the molecular tails in the air. In the X-ray diffraction studies, this has already been recognized.[8,10] However, optical microscopy methods are essentially sensitive to the ordering of the long tails of molecules. Recent Monte Carlo simulations for a system of surfactant molecules grafted at interfaces suggest that mesophases of Langmuir monolayers,

apparently intermediate between crystalline and liquid phases, are characterized by frozen crystalline heads and fluidized tails of the molecules. This coincides with an alternative view that Langmuir monolayers can be modeled by a strain field of ordered head groups and molecular tails with orientational freedom. Crystalline phases would be characterized by crystallinity of head groups and tails, while in liquid phases both head groups and molecular tails are fluidized. Melting of the quasi-two-dimensional system of a Langmuir monolayer would go through mesophases with ordered head groups. For these reasons we do not consider Langmuir monolayers as true hexatics.

We have recently proposed[12] a microscopic description of the tilt−strain coupling to frame a correlation between the nature of intermolecular interactions and the phase behavior of Langmuir monolayers. Fluctuations in molecular orientations are described in terms of surface harmonics where the variation in tilt angle is taken into account. A coupling with the elasticity of the system is described in terms of microscopic translational−rotational coupling parameters. We have treated condensed Langmuir monolayer phases as being 2-D crystalline; in particular, the LS ("superliquid") phase has been considered as the 2-D crystal of highest symmetry which serves as the parent phase for the others. This approximation allowed insight into the mechanism of instabilities which drive the phase transitions. It became evident that the orientational fluctuations described by $l = 2$ spherical harmonics trigger the shear strain elastic instabilities which are likely to drive phase transitions in the Langmuir monolayers.

This mechanism of transitions among tilted phases is essentially independent of the orientational potential with azimuthal symmetry. Moreover the phases are characterized by both strain and orientational order parameters that are related to each other through the elasticity of the system. This approach has suggested that the molecular tilt can be conveniently described by the concept of elastic dipoles embedded in an isotropic 2-D elastic medium. Their interaction makes the system ferroelastic.

Ferroelasticity commonly refers to the interaction between anisotropic defects in elastic media that become correlated through the elastic interaction of the medium which is deformed by the presence of the defects. According to our model of the Langmuir monolayer, the molecular tails, characterized by orientational degrees of freedom, are "defects" grafted onto the 2-D elastic medium with the translational order of head groups. Ferroelasticity would therefore mean a correlation of orientations of molecular tails through the elastic interaction of the translationally ordered head groups.

In this contribution we propose a description of Langmuir monolayers in terms of elasticity theory. The elastic multipoles were originally introduced as a model for the interaction of defects and impurities in a bulk solid.[13,14] They have been shown to be a very useful and elegant concept for orientational glasses[15,16] and crystals with orientational disorder.[17,18] Very recently elastic multipoles have been adopted for a theory of solid state reactions in a quantitative description of the mechanical characteristics of the reaction cavity.[19] The concept of elastic multipoles, which describe a force distribution around a molecule, is thus convenient for modeling molecular systems.

Individual molecules can be treated as objects immersed in an isotropic elastic medium. The objects are characterized by a multipole moment which is a measure of the extent to which an object embedded in the elastic medium disturbs the medium by deviating from sphericity. The model is especially suitable for molecular systems where molecular shape[20] rather than

chemical nature determines the predominant interaction and packing. It is reminiscent of the well-known "close-packing" principle commonly believed to govern the structures of simple molecular solids.

Langmuir monolayers are appropriate for modeling by elastic multipoles, and we are unaware of any other attempts to do so. Mechanical models are commonly used to mimic monolayer molecules. Most extensively studied is the model of grafted rods,[21,22] where molecules are approximated by rigid, rodlike particles grated onto a planar surface. This model has been mostly used for computer experiments.[23] However, the assumed interaction potential between the rods is often unrealistic. We intend to demonstrate how the elastic multipole concept models the Langmuir monolayer by representing the molecules as elastic multipoles and by taking the interaction between them as that between the multipoles. The model can be extended, and molecular compressibility can be introduced, which, for the amphiphilic molecules, would be a measure of aliphatic chain flexibility. This will allow inclusion of coupling between molecular tilt and chain conformation.

Following the approach proposed in the previous paper,[12] we shall treat the LS phase as a hexagonal, crystal-like phase, whose equilibrium behavior is describable by continuum elasticity theory. In section 2 we describe the energy of the system. Then in section 3, we show how translational−rotational coupling is reformulated in terms of elastic multipoles and show that the effective interaction between orientational fluctuations of molecules corresponds with the interaction of elastic multipoles. The appropriate matrix of the elastic Green's function will be calculated and transformed into a representation in spherical harmonics. In section 4 we discuss how the model of elastic multipoles in a crystalline phase can be adapted to mesophases using a coarse-graining procedure. Then we calculate the elastic properties of a Langmuir monolayer and show how the elastic dipole interaction destabilizes the hexagonal phase with vertical molecules and drives ferroelastic phase transitions.

## 2. The System and Its Energy in the Elastic Continuum Limit

We consider a 2-D system with long molecules, vertically attached to an impenetrable surface. The molecules form a structure represented by the $C_{6v}$ point group symmetry. We denote by $\mathbf{X}(k)$ the position of the $k$-th molecule on the 2-D net. This is where the head group of a molecule is attached to a supporting surface. Displacements, $\mathbf{u}(k)$, are measured with respect to the equilibrium position, $\mathbf{R}(k)$, so that $\mathbf{X}(k) = \mathbf{R}(k) + \mathbf{u}(k)$. The orientation of a molecule is given by $\Omega(k)$ which contains Euler angles for a nonlinear molecule or polar angles, $\theta$ and $\phi$, for a linear molecule (see Figure 1).

The potential energy of the system is

$$V = \frac{1}{2}\sum_k \sum_{k'} V(kk') \qquad (2.1)$$

where the molecule−molecule pair potential is

$$V(kk') = V[\mathbf{X}(k),\mathbf{X}(k');\Omega(k),\Omega(k')] \qquad (2.2)$$

We expand the potential in terms of the displacements $\mathbf{u}(k)$ according to

$$V = V^R + V^{TR} + V^T \qquad (2.3)$$

Phase Transitions in Langmuir Monolayers

*J. Phys. Chem., Vol. 100, No. 16, 1996* **6795**

where

$$V^R = \frac{1}{2}\sum_k \sum_{k'} V[\mathbf{R}(k),\mathbf{R}(k');\Omega(k),\Omega(k')] \quad (2.4)$$

$$V^{TR} = \sum_k \sum_{k'} V_i'[\mathbf{R}(k),\mathbf{R}(k');\Omega(k),\Omega(k')]u_i(k') \quad (2.5)$$

$$V^T = \frac{1}{2}\sum_k \sum_{k'} V_{ij}[\mathbf{R}(k),\mathbf{R}(k');\Omega(k),\Omega(k')]u_i(k)u_j(k') \quad (2.6)$$

The coefficients of the expansion are functions of molecular orientations and can be expressed in terms of symmetry-adapted orientational functions such as spherical harmonics for linear molecules or rotational matrices for nonlinear molecules. We shall, for simplicity, consider linear molecules and, following the arguments of Somoza and Desai,[24] take the orientational fluctuations to be described by the set[12]

$$(E_1) \quad Y_1 = (Y_{1,1} + Y_{1,-1})/\sqrt{2} = cx \quad (2.7)$$

$$(E_2) \quad Y_2 = (Y_{1,1} - Y_{1,-1})/\sqrt{2} = cy \quad (2.8)$$

$$(A_1) \quad Y_3 = Y_{2,0} = c'(2z^2 - x^2 - y^2) \quad (2.9)$$

$$(E_2) \quad Y_4 = (Y_{2,2} + Y_{2,-2})/\sqrt{2} = c''(x^2 - y^2) \quad (2.10)$$

$$(E_2) \quad Y_5 = (Y_{2,2} - Y_{2,-2})/\sqrt{2} = c''xy \quad (2.11)$$

where $c = (3/4\pi)^{1/2}$, $c' = (5/16\pi)^{1/2}$, and $c'' = (15/16\pi)^{1/2}$. Irreducible representations of the $C_{6v}$ point group are given, and the Cartesian coordinates are $x = \sin\theta\cos\phi$, $y = \sin\theta\sin\theta$, and $z = \cos\theta$. This set of surface harmonics is representative of the problem. They describe vectorial ($Y_1$ and $Y_2$) and tensorial ($Y_3$, $Y_4$, and $Y_5$) orientational fluctuations. The set of variables which we chose to describe the system is therefore $\mathbf{u}(k)$ $\{u_x, u_y\}$ for translational displacement and $Y(k)$ $\{Y_1, Y_2, Y_3, Y_4, Y_5\}$ for the orientational fluctuations.

The rotational potential, $V^R$, can now be written as

$$V^R = \frac{1}{2}\sum_k \sum_{k'} Y_\alpha(\mathbf{k}) J_{\alpha\beta}(\mathbf{kk'}) Y_\beta(\mathbf{k'}) \quad (2.12)$$

where the convention of summation over repeating indices is assumed. $J_{\alpha\beta}(\mathbf{kk'})$ forms a matrix of rotational−rotational coupling constants. The term where $(k = k')$ in the summation corresponds to the single-molecule orienting potential, $V_0^R$, which may be expressed in terms of spherical harmonics which transform as totally symmetric representations of the $C_{6v}$ point group,[12]

$$V_0^R = \alpha_0 + \sum_{\ell=2,4,\dots} \alpha_\ell Y_{\ell 0} + \sum_{\ell=6,8,\dots} \beta_\ell (Y_{\ell 6} + Y_{\ell 6})/\sqrt{2} + \dots \quad (2.13)$$

This rotational potential with a suitable choice of the parameters $\alpha_\ell$ and $\beta_\ell$ not only represents the conventional crystal field but, within the framework of the mean field approximation, can also approximate the effective orienting field.[25] In particular, the parameters can be taken as temperature dependent, *e.g.* the potential parameters obtained from Landau description. In this

case, $V^R$ is described by a function, as in eq 2.13. When the variation in tilt angle $\theta$ is neglected, as is often the case,[4−6] the potential contains only terms with $\ell = 6, 12, \dots$ and shows a periodicity in the azimuthal angle $\phi$.

The translational−rotational part of the potential, $V^{TR}$ (eq 2.5), is described by the product of the displacement of the $k'$-th molecule, $\mathbf{u}(k')$, and the *force*, $\mathbf{V}[kk';\Omega(k)]$, which depends on orientational fluctuations of the $k$-th molecule. Thus, the force represents an angular distribution of forces and can be expressed in terms of surface harmonics

$$V_i'[\mathbf{k},\mathbf{k'};\Omega(\mathbf{k})] = V_{i\alpha}(\mathbf{kk'}) Y_\alpha(\mathbf{k}) \quad (2.14)$$

where the coupling constants are evaluated at the equilibrium distance between coupling molecules

$$V_{i\alpha}(\mathbf{k},\mathbf{k'}) = \int d\Omega(\mathbf{k}) V_i'[\mathbf{k},\mathbf{k'};\Omega(\mathbf{k})] Y_\alpha(\mathbf{k}) \quad (2.15)$$

These details of translational−rotational coupling are important in a microscopic theory.[12]

Here we shall be interested in the elastic limit. To find the translational−rotational coupling in that limit, it is convenient to Fourier transform eq 2.14, with the result

$$V_i'(\mathbf{q}) = iV_{i\alpha}(\mathbf{q}) Y_\alpha(-\mathbf{q}) \quad (2.16)$$

It is possible to determine the form of the $(2 \times 5)$ coupling matrix $V(\mathbf{q})$ $\{V_{i\alpha}\}$ from the requirement that $V^{TR}$ must have full hexagonal symmetry and must be in the elastic limit[12]

$$V(\mathbf{q}) = 3a\begin{pmatrix} 0 & 0 & Aq_x & Bq_x & Bq_y \\ 0 & 0 & Aq_y & -Bq_y & Bq_x \end{pmatrix} \quad (2.17)$$

where $a$ is the hexagonal lattice constant and $A$ and $B$ are coupling constants for nearest neighbor molecules located at $(0,0)$ and $(a,0)$. The fact that there is no translational−rotational coupling for harmonics $Y_1$ and $Y_2$ indicates that forces due to translational displacements along $x$ and $y$ are balanced at equilibrium by molecular torques associated with orientational fluctuations described by $Y_1$ and $Y_2$.

The translational part of the potential, $V^T$ (eq 2.6), can be expressed in terms of the dynamical matrix $\mathbf{M}(\mathbf{q})$

$$V^T = \frac{1}{2}\sum_q u_i(\mathbf{q}) M_{ij}(\mathbf{q}) u_j(-\mathbf{q}) \quad (2.18)$$

As for the 2-D system the dynamical matrix is $(2 \times 2)$ and consists of the Fourier transform elements of force constants, $V''[\mathbf{R}(k),\mathbf{R}(k')]$. In the elastic limit, the dynamical matrix is expressed in terms of bare elastic constants, $C_{ijkl}^\circ$. For the 2-D hexagonal system the matrix reads

$$\mathbf{M}(\mathbf{q}) =$$
$$\rho^{-1}\begin{pmatrix} C_{1111}^\circ q_x^2 + C_{1212}^\circ q_y^2 & \frac{1}{2}(C_{1111}^\circ + C_{1122}^\circ)q_x q_y \\ \frac{1}{2}(C_{1111}^\circ + C_{1122}^\circ)q_x q_y & C_{1212}^\circ q_x^2 + C_{1111}^\circ q_y^2 \end{pmatrix} \quad (2.19)$$

where $m$ is the molecular mass and $\rho = m/a^2$. It is convenient and commonly accepted that the elastic constants of an isotropic elastic medium can be expressed in terms of Lame's constant, $\lambda$, and the shear modulus, $\mu$,[26]

$$C_{ijkl} = \lambda\delta_{ij}\delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \quad (2.20)$$

*e.g.*

$$C_{1111} = 2\mu + \lambda, \quad C_{1212} = \mu, \quad C_{1122} = \lambda$$

### 3. Elastic Dipoles and Their Interaction

Consider the total potential energy (eq 2.3). We define a new displacement field, $\mathbf{s}(\mathbf{q})$, such that

$$u_i(q) = s_i^{el}(\mathbf{q}) + s_i(\mathbf{q}) \qquad (3.1)$$

The first term represents the elastic displacement which minimizes the total potential and is given by

$$s_i^{el}(\mathbf{q}) = -M_{ij}^{-1}(\mathbf{q})\, V_j'(-\mathbf{q}) \qquad (3.2)$$

where $M_{ij}$ stands for the $(ij)$-th element of the inverse dynamical matrix and the force is given by eq 2.16. On substituting eq 3.2 into eq 3.1 and then calculating the total energy, we obtain

$$V = \frac{1}{2}\sum_{\mathbf{q}} s(\mathbf{q})\, M(\mathbf{q})\, s(\mathbf{q}) + V^R + V_{ind} \qquad (3.3)$$

Where the *indirect* rotational interaction is defined as

$$V_{ind} = -\frac{1}{2}\sum_{\mathbf{k}}\sum_{\mathbf{k'}} Y_\alpha(\mathbf{k})\, W_{\alpha\beta}(\mathbf{kk'})\, Y_\beta(\mathbf{k'}) \qquad (3.4)$$

This indirect coupling between orientational fluctuations is mediated by translational degrees of freedom and is given explicitly as

$$W_{\alpha\beta}(\mathbf{kk'}) = N^{-1}\sum_{\mathbf{q}} L_{\alpha\beta}(\mathbf{q})\, \exp i\mathbf{q}\,[\mathbf{R}(k) - \mathbf{R}(k')] \quad (3.5)$$

with

$$L_{\alpha\beta}(\mathbf{q}) = V_{\alpha i}(\mathbf{q})\, M_{ij}^{-1}(\mathbf{q})\, V_{j\beta}(-\mathbf{q}) \qquad (3.6)$$

Our main concern is to calculate the indirect rotational interaction mediated by the elasticity of the system. It follows from eq 3.3 that the orientational stability of the system is determined by the total orientational potential, $V^R + V_{ind}$. This potential will be highly anisotropic because of the *indirect* interaction coupling, $W(\mathbf{kk'})$, which depends not only on the distance between the molecules but also on the direction of the vector, $\mathbf{R}(k) - \mathbf{R}(k')$. It is most conveniently presented in the framework of elasticity theory.

We rewrite eq 2.16 in the form

$$V_i'(\mathbf{q}) = iN^{-1/2}\sum_{k} P_{ij}(\mathbf{k})q_j \exp i\mathbf{q}\,\mathbf{R}(k) \qquad (3.7)$$

where we have used the elastic limit of the translational−rotational coupling and the Fourier transform of the surface harmonics. We define

$$P_{ij}(\mathbf{k}) = a_{ij}^\alpha A_\alpha Y_\alpha(\mathbf{k}) \qquad (3.8)$$

as the *elastic dipole* of the $k$-th molecule induced by orientational fluctuations specified by the surface harmonics. $A_\alpha$ equals $A$ for $\alpha = 3$, equals $B$ for $\alpha = 4$ or $5$, and represents the translational−rotational coupling constants (see eq 2.17). $a_{ij}^\alpha$ are elements of real, spherical unit tensors.[14] On writing eq 3.7 we have represented a force distribution around a reorienting molecule, $k$, by an elastic dipole.

On using eq 3.7, we can write the translational−rotational part of the energy (eq 2.5) as

$$V^{TR} = iN^{-1/2}\sum_{\mathbf{q}} u_i(\mathbf{q})\sum_{k} P_{ij}(\mathbf{k})q_j \exp i\mathbf{q}\,\mathbf{R}(k) \qquad (3.9)$$

The strain tensor components defined as

$$e_{ij}(\mathbf{k}) = \frac{1}{2}\left(\frac{\partial u_i(\mathbf{k})}{\partial R_j(\mathbf{k})} + \frac{\partial u_j(\mathbf{k})}{\partial R_i(\mathbf{k})}\right) \qquad (3.10)$$

when calculated from the Fourier transform of the translational displacement, $\mathbf{u}(q)$, can be used to write eq 3.9 in the compact form

$$V^{TR} = \sum_{k} e_{ij}(\mathbf{k})\, P_{ij}(\mathbf{k}) \qquad (3.11)$$

This shows that the translational−rotational part of the energy is conveniently represented as a sum over sites of products: local strain times local stress. Further, it gives a simple interpretation of an elastic dipole in a monolayer film as a local stress generated by a molecular tilt.

As in elasticity theory, we defined the elastic Green's function[26]

$$G_{ij}(\mathbf{kk'}) = \sum_{q} M_{ij}^{-1}(\mathbf{q})\, \exp i\mathbf{q}\,[\mathbf{R}(k) - \mathbf{R}(k')] \quad (3.12)$$

which satisfies the relation $G_{ij}(\mathbf{kk'})\, M_{il}(\mathbf{k'k''}) = \delta_{il}(\mathbf{kk''})$. We can express elastic displacement and local strain as follows,

$$s_i^{el}(\mathbf{k}) = G_{ijk}(\mathbf{kk'})\, P_{jk}(\mathbf{k'}) \qquad (3.13)$$

$$e_{ij}(\mathbf{k}) = G_{ijkl}(\mathbf{kk'})\, P_{kl}(\mathbf{k'}) \qquad (3.14)$$

where the nonlocal response functions are corresponding derivatives of the Green's function, as for example

$$G_{ijkl}(\mathbf{kk'}) = \frac{\partial^2}{\partial \mathbf{R}_j(k)\, \partial \mathbf{R}_l(k')} G_{ik}(\mathbf{kk'}) \qquad (3.15)$$

Relation 3.14 implies that the above response function can be identified as a nonlocal *compliance*. With this association, we write

$$V_{ind} = -\frac{1}{2}\sum_{\mathbf{k}}\sum_{\mathbf{k'}} P_{ij}(\mathbf{k})\, G_{ijkl}(\mathbf{kk'})\, P_{kl}(\mathbf{k'}) \qquad (3.16)$$

This indicates that the indirect rotational energy is the lattice deformation energy due to local stresses induced by the reorientation of molecules. In this equation, the summation runs over all molecular sites and includes the term $\mathbf{k} = \mathbf{k'}$, which is the energy of creation of an elastic dipole in the elastic medium, $E_C$. The energy is $E_C = P_{ij}S_{ijkl}^0 P_{kl}$, where $S^0 = (C^0)^{-1}$ is the bare elastic compliance tensor.

The elastic Green's function for a 2-D hexagonal (isotropic) system can be calculated following the procedure in ref 2 with the result

$$G_{ij}(\mathbf{kk'}) = -[4\pi\mu(2\mu + \lambda)]^{-1}[(3\mu + \lambda)\delta_{ij} \ln R - (\mu + \lambda)c_i c_j] \quad (3.17)$$

where $R = |\mathbf{R}(k) - \mathbf{R}(k')|/a$ and $c_i = R_i/R$. We calculate the elastic coupling between the dipoles (eq 3.15)

$$G_{ijkl}(\mathbf{kk'}) = [4\pi\mu(2\mu + \lambda)]^{-1}R^{-2}\{(3\mu + \lambda)[\delta_{ik}\delta_{jl} - 2c_j c_l \delta_{ik}] - (\mu + \lambda)[\delta_{il}\delta_{kj} + \delta_{ij}\delta_{kl} - 2(\delta_{ij}c_k c_l + \delta_{kj}c_i c_l + \delta_{jl}c_i c_k + \delta_{il}c_k c_j - \delta_{kl}c_i c_j) + 8c_i c_j c_k c_l]\} \quad (3.18)$$

It is convenient to represent the indirect interaction (eq 3.16) in spherical coordinates rather than Cartesian ones. We split

Phase Transitions in Langmuir Monolayers

*J. Phys. Chem., Vol. 100, No. 16, 1996* **6797**

the elastic dipoles into components, $P_{ij} = a_{ij}^\alpha P_\alpha$, where $P_\alpha = A_\alpha Y_\alpha$ defines the transformed couplings between dipoles

$$G_{\alpha\beta}(\mathbf{k}\mathbf{k}') = a_{ij}^\alpha G_{ijkl}(\mathbf{k}\mathbf{k}') a_{kl}^\beta \qquad (3.19)$$

with the transformed elastic compliance

$$S_{\alpha\beta}^0 = a_{ij}^\alpha S_{ijkl}^0 a_{kl}^\beta \qquad (3.20)$$

The indirect interaction

$$V_{\text{ind}} = -\frac{1}{2} \sum_{\mathbf{k} \neq \mathbf{k}'} \sum P_\alpha(\mathbf{k})[N^{-1}S_{\alpha\beta}^0 + G_{\alpha\beta}(\mathbf{k}\mathbf{k}')]P_\beta(\mathbf{k}') \qquad (3.21)$$

is highly anisotropic. To see this, we consider interaction of two elastic dipoles separated by the vector $\mathbf{R}$ in the direction of the $x$-axis. The result is

$$V_{\text{ind}}(\mathbf{R}||x) = -(4\mu)^{-1}\frac{2\mu + \lambda}{\mu + \lambda}\left[1 + \frac{2\mu(\mu + \lambda)}{\pi(2\mu + \lambda)^2 R^2}\right] \times$$

$$(A + B)^2[Y_3(0) + Y_4(0)][Y_3(R) + Y_4(R)] -$$

$$\frac{\lambda}{\mu + \lambda}\left[1 + \frac{(2\mu + 3\lambda)(\mu + \lambda)}{\pi(2\mu + \lambda)\lambda R^2}\right](A - B)^2 \times$$

$$[Y_3(0) - Y_4(0)][Y_3(R) - Y_4(R)] +$$

$$\left[1 + \frac{(5\mu + 3\lambda)}{4\pi(2\mu + \lambda)R^2}\right]B^2 Y_5(0)\, Y_5(R) \quad (3.22)$$

It is convenient to use the linear combination $[Y_3 + Y_4]/2$ for the $(xx)$ component of the elastic dipole and $[Y_3 - Y_4]/2$ for its $(yy)$ component. We conclude that the tilt of molecules in the direction perpendicular to the vector $\mathbf{R}$ is highly unlikely, as shown by the second term, and the molecules will tend to tilt in the direction of the vector which joins them. This supports the analogy to the interaction of electric dipoles where a "head-to-tail" orientation is favored over a parallel arrangement of dipoles. This can be further extended by considering elastic compliance as an analog of the macroscopic dielectric constant and the nonlocal compliance as corresponding to the dielectric function.

Now we can calculate the indirect potential for a system of hexagonal symmetry. The summation over interacting nearest neighbors, which are at distance $R$, gives

$$V_{\text{ind}}(R) =$$

$$-\frac{1}{2(\mu + \lambda)}\left[1 + \frac{6(\mu^2 - \lambda^2)}{\pi\mu(2\mu + \lambda)R^2}\right]A^2[3\cos^2\theta(0) - 1] \times$$

$$[3\cos^2\theta(R) - 1] - \frac{1}{2\mu}\left[1 + \frac{3(\mu - \lambda)}{4\pi(2\mu + \lambda)R}\right]B^2 \times$$

$$\sin^2\theta(0)\sin^2\theta(R)\cos 2[\phi(0) - \phi(R)] \quad (3.23)$$

This equation gives two contributions to the total energy of a system (eq 3.3). The indirect potential should be understood as the change of energy of the system with respect to the energy of the 2-D elastic medium, because surfactant molecules are long and oriented at the interface. The first term in the indirect potential gives the interaction of the elastic dipole components $(zz)$ along the long axes of molecules forming the Langmuir monolayer. By the very nature of the system, where molecules are oriented at the water−air interface, this term is nonzero and largest for a phase with vertical molecules. The second term describes the interaction of the $(xx)$ and $(yy)$ components of the

elastic dipoles which are related to effective cross sections of the molecules. This term favors tilting of the molecules.

For $\mu = \lambda$, which corresponds to the Cauchy relation between elastic constants, and when there are only central forces between molecules, the indirect interactions in the hexagonal system are $R$-independent. Moreover, while the energy is independent of the tilt direction of molecules, it does prefer them to be tilted, $\theta \neq 0$. However, for the general case, as long as $[(8\pi + 3)\mu + (4\pi - 3)\lambda] > 0$, the elastic dipole interaction prefers the molecules to be tilted in such a way as to maintain the smallest difference between tilted directions of neighboring molecules. This tendency may change, depending on the elastic properties of the system, and in particular, the interaction is critically dependent on the shear modulus, $\mu$, and is important for soft systems. When the system reaches an elastic instability ($\mu \Rightarrow 0$), the interaction becomes extremely attractive provided the translational−rotational coupling constants, $A$ and $B$, are nonzero. If the elastic instability drives the system toward melting, the couplings diminish as well (*i.e.*, there is no static translational−rotational coupling in an isotropic liquid), and the elastic dipole interaction does not influence the collective orientation of the molecules. However, the elastic instability, $\mu \Rightarrow 0$, might drive a transition toward a solid phase or mesophase, where the coupling still exists. Then the elastic dipole interaction becomes attractive to the extent that it overcomes direct rotational interactions and leads to a collective tilt of the molecules. This creates a new phase, a ferroelastic phase, with correlated (ordered) elastic dipoles.

## 4. Mesoscopic Approximation

We now analyze how results are modified when one considers mesophases instead of a system with long-range translational order. Following an approach adopted for the glassy state,[24] we shall use the microscopic Hamiltonian from section 2 as a guideline for a phenomenological coarse-graining procedure. There are reasons why such a phenomenological procedure is needed. A mesophase is characterized by large fluctuations, predominantly in translational displacements on microscopic length scales. Therefore, standard procedures to extract elastic properties (*e.g.* by gradient expansions) cannot be used here. Secondly, the reorientation of a molecule in a translationally disordered system is a strongly anharmonic process on microscopic length scales. It is hard to estimate it from first principles.

In a mesophase we consider thermodynamic parameters for regions where the correlation length $\xi$ of thermal orientational fluctuations is much larger than the NN distance; *i.e.*, $\xi \gg a$. The coarse-graining procedure should lead to an effective Hamiltonian for long-wavelength fluctuations. The form of $H_{\text{eff}}$ is restricted by the following simplifying assumptions: (i) The range of all direct intermolecular forces is short compared to the mesoscopic coarse-graining length $\xi_0$ ($a < \xi_0 < \xi$) with the possible exception of direct interactions between molecules due to electrical multipoles. This assumption is well satisfied for Langmuir monolayers where the predominant interaction is between aliphatic chains and is of short range. As a consequence of this assumption, $H_{\text{eff}}$ should consist of terms and their derivatives which are *local* in a coarse-grained displacement field, $\mathbf{u}(x)$. (ii) On mesoscopic length scales, the system behaves as an elastic medium so that $H_{\text{eff}}$ is at most quadratic in $\mathbf{u}(x)$. This does not imply the harmonic approximation at shorter length scales, where a system with translational disorder, such as a mesophase, is anharmonic in molecular displacements. (iii) The coarse-graining procedure divides the system into *meso-*

*scopic* grains of size $\xi_0$. Within a grain, the system is considered to possess hexagonal $C_{6v}$ point group symmetry.

Given these three simplifying assumptions, the simplest effective Hamiltonian takes the form

$$H_{\text{eff}} = \sum_x \left( \frac{1}{2} e_{ij}(x) C^0_{ijkl} e_{kl}(x) + P_{ij}[\Omega(x)] e_{ij}(x) \right) + \frac{1}{2} \sum_x \sum_x V^R[\Omega(x), \Omega(x')] \quad (4.1)$$

The summation extends over the points of a coarse-grained 2-D net with hexagonal $C_{6v}$ point group symmetry. The three terms can be identified as corresponding to the microscopic terms. In particular, the second term corresponds to eq 3.11. The stress on the mesoscopic length scale, $\mathbf{P}[\Omega(x)]$, depends on the orientation of molecules within the grain $x$ and is expressed in terms of spherical harmonics. The elastic constants are those on the mesoscopic coarse-graining scale. The direct rotational potential can be decomposed into a potential which denotes local orientational anisotropy, $V^R_0[\Omega(x)]$, and coupling ($x \neq x'$). The coupling between grains will, in general, contain contributions from direct electrical multipole interactions as well as indirect interactions mediated by lattice distortions on the short length scales, $l < \xi_0$. For the Langmuir monolayers, the coupling in the effective Hamiltonian (eq 4.1) is essentially the indirect interaction, $V_{\text{ind}}$, as found in the previous section.

The thermodynamic properties of the model can be obtained from the partition function with the Hamiltonian, $H_{\text{eff}}$, by integrating over $e(x)$ and $\Omega(x)$. It is convenient to decompose the strain into a homogeneous part, $\epsilon$, and an inhomogeneous one: $e(x) = \epsilon + \delta e(x)$. Minimization of the partition function with respect to homogeneous strain gives

$$N^{-1} \sum_r \langle P_{ij}(x) \rangle = C^0_{ijkl} \langle \epsilon_{kl} \rangle \quad (4.2)$$

where, as follows from eq 3.8, $\langle P_{ij}(x) \rangle = a^\alpha_{ij} A_a \langle Y_a(x) \rangle$. The orientationally ordered phase ($\langle Y_\alpha \rangle = 0$) is always accompanied by a homogeneous deformation which is characteristic of ferroelasticity. This is a deformation of the 2-D elastic medium formed by the head groups, and eq 4.2 demonstrates that Langmuir monolayers with orientationally ordered molecules (tails) are always strained 2-D systems. In particular, for the phase with vertical molecular tails, $\langle Y_\alpha \rangle \neq 0$, and consequently from eq 4.2, the totally symmetric strain ($e_{11} + e_{22}) \neq 0$. If this phase were to serve as a reference for a Landau free energy expansion, $\langle Y_\alpha \rangle$ should not be considered as the orientational order parameter. However, if the reference state is the 2-D elastic medium of the molecular head groups, eq 4.2 gives the linear relation between the orientational order parameter, $\langle Y_\alpha \rangle$, and macroscopic strain.

If the orientations occurring within grains are frozen into random directions such that $\sum_x \langle P_{ij}(x) \rangle = 0$, which corresponds to fluidized molecular tails, while the head groups are frozen in a crystalline arrangement, the macroscopic deformation vanishes, and there are randomly frozen inhomogeneous strains, $\delta e(x)$, within every grain. This can be found by minimization of the partition function with respect to displacement, $\mathbf{u}(x)$. One gets

$$\langle u_i(x) \rangle = \sum_{x'} G_{ij}(xx') \left( \frac{\partial \langle P_{jk}(x') \rangle}{\partial x_k'} \right) \quad (4.3)$$

Inhomogeneous strain can be calculated from eq 3.10. The elastic Green's function is that calculated in section 3, since

the elastic 2-D medium is a crystalline arrangement of head groups, and the derivative of the elastic dipole represents an average force induced by tilted molecules within grain $x'$ acting on the grain at $x$. The inhomogeneous strain vanishes when averaged over all grains of the system. Langmuir monolayers with such frozen inhomogeneous strains are reminiscent of an orientational glassy state.

## 5. Ferroelasticity of Langmuir Monolayers

The above discussion demonstrates that Langmuir monolayers are excellent candidates for ferroelastic behavior. By this we mean a strain reversal process that can be driven by a change in orientation of the molecular tails. The ferroelastic phase is characterized, therefore, by an average strain, $\langle \epsilon \rangle$, and average orientational fluctuations, $\langle Y_\alpha \rangle$. These can be considered as the order parameters for the system if the reference state is the 2-D elastic medium of the head groups. Due to the strain−molecular reorientation coupling, the bare elastic constants, $C^0$, of the medium are renormalized to their observed values, $C$. The elastic compliance, $S = (C)^{-1}$, defined as the matrix of second derivatives of the free energy with respect to externally applied homogeneous stress is

$$S_{ijkl} = \beta N^{-1} [\langle \epsilon_{ij} \epsilon_{kl} \rangle - \langle \epsilon_{ij} \rangle \langle \epsilon_{kl} \rangle] \quad (5.1)$$

The thermodynamical averages are calculated with $H_{\text{eff}}$ (eq 4.1) using a decomposition of strain into homogeneous and inhomogeneous parts and a shift of variables, $\epsilon' = \epsilon + (C^0)^{-1} \sum_x \mathbf{P}(x)$. The result is

$$S = S^0 + [S^0 \mathbf{a}^\alpha A_\alpha]^T X_{\alpha\beta} [S^0 \mathbf{a}^\beta A_\beta] \quad (5.2)$$

where $S^0$ is the bare compliance tensor and $\mathbf{a}^\alpha$ is the real spherical unit matrix. The rotational susceptibility is

$$X_{\alpha\beta} = N^{-1} \sum_x \sum_{x'} X_{\alpha\beta}(x,x') \quad (5.3)$$

where

$$X_{\alpha\beta}(x,x') = \beta \langle Y_\alpha(x) \, Y_\beta(x') \rangle \quad (5.4)$$

The susceptibility in eq 5.3 has to be calculated for every system for which the rotational part of the system Hamiltonian has been specified. This has been discussed in ref 11.

Here, we shall consider the simplest approximation for the rotational suceptibility in two limits, $x = x'$ and $(x - x') \Rightarrow \infty$, to get a rough estimation of the effect. Neglecting the direct rotational potential, the on-site susceptibility is simply $X_{\alpha\alpha} = \beta$. In the limit of an infinite distance, the interaction of two orientational fluctuations is equal to the deformation energy. We write for the approximate rotational susceptibility of the system

$$X_{\alpha\alpha} = [\beta^{-1} - A_\alpha^2 S^0_{\alpha\alpha}]^{-1} \quad (5.5)$$

As a property of a system, the susceptibility has to be invariant with respect to hexagonal symmetry. Thus, there are only diagonal elements in this representation. $S^0_{\alpha\alpha}$ is the elastic compliance expressed in coordinates of spherical harmonics; see eq 3.21. Although it represents an oversimplified version of the rotational susceptibility, eq 5.5 gives a plausible interpretation of an incipient instability. For temperatures when the thermal energy is greater than the elastic dipole deformation energy, the susceptibility is positive and finite, indicating that the system is stable with respect to orientational fluctuations

Phase Transitions in Langmuir Monolayers

*J. Phys. Chem., Vol. 100, No. 16, 1996* **6799**

described by $Y_\alpha$. When the temperature decreases, however, the deformation energy overcomes the thermal energy and the system becomes orientationally unstable, $X_{\alpha\alpha} \Rightarrow \infty$. As long as there is enough thermal energy to create elastic dipoles, the system is stable. If, however, the thermal energy is not sufficient to form the elastic dipoles, the system tends toward a structural change in order to gain enough energy for their creation (reoriented molecules). This structural change is driven by an elastic instability, as seen from the equation

$$S_{\alpha\alpha} = S^0_{\alpha\alpha}[1 + \{k_BT/E_\alpha - 1\}^{-1}] \qquad (5.6)$$

where $E_\alpha = A^0_\alpha S^0_{\alpha\alpha}$ represents the energy of deformation due to interaction of two elastic dipoles of type $\alpha$.

In particular, we seek a renormalization of the shear modulus

$$\mu = \mu^0[1 + \{\mu^0 k_B T A_4^{-2} - 1\}^{-1}]^{-1} \qquad (5.7)$$

For $k_BT = B^2(\mu^0)^{-1}$, $\mu$ vanishes and leads to a distorted system in which there is nonzero strain and the molecular tilt direction is expressed in terms of elastic dipoles

$$\langle e_{12} \rangle = -(2\mu^0)^{-1}\langle P_{12} \rangle \propto \langle \sin 2\phi \rangle \qquad (5.8)$$

$$\langle e_{11} - e_{22} \rangle = -(2\mu^0)^{-1}\langle P_{11} - P_{22} \rangle \propto \langle \cos 2\phi \rangle \quad (5.9)$$

The distorted hexagonal structures measured by the strains given by eqs 5.7 and 5.8 represent oblique and rectangular lattices, respectively. The sign of the strains is determined by the microscopic translational−rotational constant, $B$, which is determined by the microscopic nature of intermolecular interactions and by the tilt direction angle, $\phi$. For positive elastic dipoles the deformation is reflected by contraction (negative strain) and vice versa.

The essence of ferroelasticity is that one can stimulate a strain reversal by changing the orientation of molecules. This implies that the opposite process is also possible. The strain reversal as a function of azimuthal tilt angle is seen from the angle dependence of the elastic dipoles. Phases with tilt toward NN and NNN are *ferroelastic* domains within a phase which results from an orientational instability against $Y_4$ fluctuations. It follows that, for example, the "swiveling" transition between NN and NNN phases[27] proceeds through the unstable state of vertical molecules on the hexagonal net. This mechanism allows the molecules to rotate around their long axes in the process, which is what has been observed.[27] Moreover, because both strains, $\langle e_{12} \rangle$ and $\langle e_{11} - e_{22} \rangle$, are induced by the same elastic instability, a tilted phase may, in general, be a mixture of all those domains if there is no external (uniaxial) stress applied to the system. Under experimental conditions for Langmuir monolayers, this is difficult to achieve. Therefore, some preference for the existence of ferroelastic domains will be forced. With the concept of elastic dipoles, this can be analyzed for a particular experiment.

## 6. Conclusions

This study has demonstrated that it is both useful and helpful to model tilted molecules in Langmuir monolayers by elastic dipoles. These model orientational degrees of freedom of the molecular tails and are local stresses expressed by expectation values of spherical harmonics with $/= 2$, and their strength is given by translational−rotational coupling constants. The stresses interact with each other through the elastic field of the monolayer, which is a 2-D elastic medium of molecular head groups arranged on the water surface. The deformation energy

is an indirect interaction between orientational fluctuations. This yields two important results.

The interaction of reorienting molecules can be modeled by the interaction of elastic dipoles. The potential, with parameters directly dependent on the elastic constants, has been obtained for the 2-D hexagonal lattice. This may prove useful for computer experiments on these systems. The concept of elastic dipoles also allows representation of an amphiphilic molecule as a set of segments where an elastic dipole can be assigned to each. This approach allows modeling of intermolecular forces as interactions of segments of elastic dipoles, thereby allowing inclusion of the molecular compressibility as well as the elastic properties of the system.

When the elastic dipoles' interaction is strong enough, they will order, leading to an orientational order of the molecules. The direct relation between the tilt and strain suggests that the ordered phase is ferroelastic where domains with different orientations are characterized by different strains. In particular, the angular distributions in terms of the tilt-azimuthal angle, $\phi$, of the macroscopic shear strain, $e_{12}$, have the symmetry of the $Y_5$ harmonics and that for $(e_{11} - e_{22})$ is of $Y_4$ symmetry. We conclude that the Langmuir monolayer phases with tilts toward NN and NNN are ferroelastic domains and that a tilted phase can in general be a mixture of such domains. Within this concept, the "swiveling" transition between NN and NNN phases is seen as a strain reversal process which goes through a state of the undeformed hexagonal lattice. This result strongly suggests that monolayer textures may be characterized quantitatively and on a microscopic scale by models based upon elastic multipoles and their mediation by the film itself.

This study demonstrates the efficacy of applying analyses based on solid state theory to understanding the phase behavior of molecular monolayers. In particular, the approach permits a direct identification of processes that occur in the Langmuir films with well-known phenomena observed in solids. The elastic properties of the monolayers provide an extensive arena for investigating these commonalities and, coupled with appropriate design of the amphiphiles based on these models, may be utilized to provide novel films with desirable materials properties.

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