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David R. Swanson Technical University of Wroclaw, Wroclaw, Poland

Tadeusz Luty Technical University of Wroclaw, Wroclaw, Poland

Craig J. Eckhardt University of Nebraska - Lincoln, ceckhardt1@unl.edu

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Langmuir monolayers as disordered solids: Strain-state calculations applied to stearic acid

David R. Swanson and Tadeusz Luty

Institute of Physical and Theoretical Chemistry, Technical University of Wroclaw, Wroclaw, Poland

Craig J. Eckhardt

Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska 68588-0304

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This paper presents a calculational procedure to determine the equilibrium phase for a given surface pressure π . The monolayer is treated as orientationally free tails grafted to a two-dimensional net formed by the head groups of the amphiphilic molecules. The head groups form a subsystem with translational degrees of freedom characterized by strain variables in the plane of the surface, and the tail groups compose a subsystem characterized by rotational degrees of freedom. The order in the monolayer derives indirectly from the crystalline head groups through translational–rotational coupling. A stress–strain relation is derived which shows the energetically most favorable path for reorientation of the molecules due to a two-dimensional strain. This set of strain states for a given symmetry (phase) allows a contribution to the strain-state partition function to be computed. It is then straightforward to calculate the strain-state contribution to the free energy for a given phase and estimate the transition temperature between phases. © 1997 American Institute of Physics. [S0021-9606(97)50928-7]

I. INTRODUCTION

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Langmuir monolayers have received considerable attention from researchers for their potential application as molecular assemblies and their present utility as quasi-twodimensional model systems. These monolayers are formed by spreading amphiphilic molecules on an aqueous surface and subsequently applying a lateral force, resulting in conformational, orientational, and translational order of various degrees. The amount of order of various phases depends crucially upon the temperature *T* and surface pressure π .^{1,2}

Langmuir monolayers may be considered to be ordered liquids, and various phases have been compared to liquidcrystalline counterparts.¹ Alternatively, these systems have been compared to molecular crystals of aliphatic chains,³ which exhibit a high degree of translational order with varying degrees of orientational order. There is ongoing discussion as to the nature of various phases reported in the literature, but certain general features are consistently found.^{1,2,4–8} At low temperature and high surface pressure there exists a crystalline phase with two molecules per unit cell aligned along the film normal, as evidenced by Davydov splitting.⁸ At low surface pressure the amphiphiles exhibit nearestneighbor tilt (NN), while at intermediate pressure next nearest-neighbor tilt (NNN) is observed. The details of the surface pressure area (πA) phase diagram are influenced by the subphase composition (pH and ionic composition),⁹ the molecular structure (length and head group),^{1,2,8} and the method used to apply pressure.⁴

This paper presents a calculational procedure to determine the equilibrium phase for a given surface pressure π . As a model system we have chosen stearic acid monolayers, due to their prominence in these systems. In short, the monolayer is treated as orientationally free tails grafted to a twodimensional net formed by the head groups of the am-

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phiphilic molecules. The head groups form a subsystem with translational degrees of freedom in the plane of the surface, and the tail groups compose a subsystem characterized by rotational degrees of freedom. The order in the monolayer derives indirectly from the crystalline head groups through translational–rotational coupling. The remainder of the paper is in four parts. First, the model is briefly reviewed. Second, the calculational procedure is described in more detail and applied to a fatty acid monolayer. The results are contained in the next section, and the final section contains discussion and conclusions concerning this method and fatty acid monolayer phases.

II. MODEL

The model is essentially that which was published previously.¹⁰ The orientational variables ({ Ω }) of the tail subsystem may be either Euler angles or spherical harmonics,^{10,11} which are more appropriate dynamical variables for the large fluctuations exhibited by these systems. It is convenient to describe the translational subsystem via strain variables ({ ε }) appropriate to a given two-dimensional lattice. The energy of such a system may be written:

$$V(\{\varepsilon\},\{\Omega\}) = V^{R}(\{\Omega\}) + V^{TR}(\{\varepsilon\},\{\Omega\}) + V^{T}(\{\varepsilon\}), \quad (1)$$

where the first term is the contribution from the orientational degrees of freedom, the third is the contribution from the translational degrees of freedom, and the second term represents the coupling between these two types of variables.

The translational contribution to the energy in Eq. (1) may be written

$$V^{T}(\{\varepsilon\}) = V^{T}_{H}(\{\varepsilon\}) + V^{T}_{T}(\{\varepsilon\}),$$

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where the first term denotes contributions from the head groups, and the second from the tails. The translational energy contribution of the tails is crucial to the determination of the global energy minimum and to subsequent local minimizations with respect to the area. The head-group contribution is not directly calculated, but is instead attributed to a rescaling of the translational energy by a πA contribution to the total energy. Nonetheless, the translational variables remain two dimensional even when including tail interactions; there are no translations allowed along the film normal. The total system may be considered as a connected stack of two-dimensional subsystems consisting of various cross sections of the film.

The orientational fluctuations are expected to follow, or quickly reach equilibrium, for a particular set of strains. The above energy may therefore be minimized with respect to Ω (dropping the brackets indicating a set of variables),

$$\left(\frac{\partial V(\varepsilon,\Omega)}{\partial\Omega}\right)_{\varepsilon} = V_c'(\varepsilon,\Omega^*) + V_{\Omega}'(\Omega^*) = 0, \qquad (2)$$

and the resulting expression solved for $\Omega^*(\varepsilon)$, the equilibrium orientation, which minimizes the energy in Eq. (1). The solution $\Omega^*(\varepsilon)$, which is a type of stress-strain relation, shows the energetically most favorable path for reorientation of the molecules due to a two-dimensional strain. The energy along this path was investigated.

II. METHOD

A. Summary

Intermolecular interactions between the tail groups are calculated as for rigid molecules using 6-exp atom-atom potentials.¹² This is a reasonable approximation for condensed phases, supported by the fact that tilt of the molecule as a whole is shown experimentally to be preferred over conformational rearrangement for these systems.⁸ Head group and surface interactions are not directly calculated, but are not ignored. Surface interactions are implied since the molecules are constrained to a plane,¹³ and head group interactions are implicit in the value of the strain variables chosen. These may be rescaled by adding a surface pressure area (πA) term to the potential energy.¹⁴ Using geometrical parameters appropriate for a fatty acid molecule, it can be shown that the two-dimensional Gibbs free energy (πA) contribution from a surface tension of 1 mN/m is of the order of that from a three-dimensional pressure of 1 kbar.

The calculated procedure consists of several steps, as follows:

- (1) The global minimum with respect to all strain and orientational variables is determined. All lattice parameters and orientational degrees of freedom are minimized. This involved minimizing a structure with an assumed fatty acid molecular structure¹⁵ in a two-dimensional crystal with either one or two molecules per unit cell.
- (2) Strain states relative to this global minimum are calculated. This is done by utilizing the dependence of the

strain on the lattice parameters, as is described below. The states calculated depend on the symmetry of the particular system investigated.

- (3) The symmetries (phases) of the states from step 2 are determined. It was found in every case presented here that the phase space may be separated into various partitions, characterized by a specific symmetry as determined by a set of orientational variables.
- (4) A complete set of strain states for each symmetry (phase) is calculated, meaning the energy V(Ω*(ε)) is determined for the most important set of strain variables.

Once the above has been completed, a contribution to the strain-state partition function¹⁶ may be computed for each phase from step 3 according to $Q^{\varepsilon} = \sum_{\text{all } \varepsilon} \exp (-\beta V(\Omega^*(\varepsilon)))$, where $\beta = 1/kT$, and k is the Boltzmann constant. It is then straightforward to calculate the strain state contribution to the free energy for a given phase as $F^{\varepsilon} = (1/\beta) \ln Q^{\varepsilon}$. A plot of this free energy versus temperature gives an estimate of the transition temperature between phases.

B. Variables

Combinations of three two-dimensional strains e_{xx} , e_{yy} , and e_{xy} were considered in this work. The latter is a pure shear strain and is denoted as ε_6 to be compatible with Voigt notation. $e_{xx} + e_{yy}$ is proportional to the change in area and is defined as ε_1 . This leaves $\varepsilon_2 = e_{xx} - e_{yy}$ as the remaining strain variable. It is straightforward to express the strain variables in terms of the lattice parameters.¹⁷ The third dimension is not relevant to the present model, and so the equations for the present model reduce to

$$e_{xx} = \frac{a_1 \sin \gamma_1^*}{a_0 \sin \gamma_0^*} - 1,$$

$$e_{yy} = \frac{b_1}{b_0} - 1,$$

$$e_{xy} = \frac{1}{2} \left[\frac{b_1 \cot \gamma_0^*}{b_0} - \frac{a_1 \cos \gamma_1^*}{a_0 \sin \gamma_0^*} \right]$$

where *a* and *b* are the lengths of the lattice vectors and γ^* is the angle between the lattice vectors in reciprocal space. The subscripts 0 and 1 denote before and after deformation, respectively.

The strain variables introduced above take the following form for a hexagonal (C_{6v}) reference cell:

$$\varepsilon_{1} = e_{xx} + e_{yy} = \frac{1}{a_{0}} \left[\frac{2}{\sqrt{3}} a_{1} \sin \gamma_{1}^{*} + b_{1} \right] - 2,$$

$$\varepsilon_{2} = e_{xx} - e_{yy} = \frac{1}{a_{0}} \left[\frac{2}{\sqrt{3}} a_{1} \sin \gamma_{1}^{*} - b_{1} \right],$$
(3)

$$\varepsilon_{6} = e_{xy} = \frac{1}{2\sqrt{3}a_{0}} [b_{1} - 2a_{1} \cos \gamma_{1}^{*}].$$

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TABLE I.	Results	for	calcu	lated	phases.
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Phase	Energy (kcal/mol)	Area/molecule (sq. angstroms)	A (angstroms)	B (angstrom)	γ (degrees)
Vertical (1 mol/u.c.) Herring hone (ng)	-26.31 -26.27	18.28 18.32	4.30 5.03	4.58 7.29	112.00
Tilted (1 mol/u.c.)	-26.01	19.09	4.70	5.29	129.76
Tilted antiparallel (pm)	-25.89	18.95	5.15	7.41	96.73

For two molecules per unit cell, the reference state chosen is centered rectangular, and the strain variables are of the form:

$$\varepsilon_{1} = e_{xx} + e_{yy} = \frac{1}{a_{0}} [a_{1} \sin \gamma_{1}^{*} + b_{1}] - 2,$$

$$\varepsilon_{2} = e_{xx} - e_{yy} = \frac{1}{a_{0}} [a_{1} \sin \gamma_{1}^{*} - b_{1}],$$

$$\varepsilon_{6} = e_{xy} = -\frac{1}{2} \left[\frac{a_{1}}{a_{0}} \cos \gamma_{1}^{*} \right].$$

For either reference state described above, three variables must be specified. This is done by scanning ε_2 and ε_6 relative to the global minimum, and minimizing the energy for these various states with respect to ε_1 (and the three orientational variables). In other words, the area of the minimized system provides the third necessary constraint. This is implemented by letting $a = a(\gamma)$ and $b = b(\gamma)$, according to the equations above, and minimizing the lattice with respect to the one remaining independent variable γ .

Though the appropriate dynamical orientational variables for these systems are spherical harmonics, these calculations involve only direct minimization, and so three orientational angles were used. The angles chosen were R_x , R_y , and R_z , or rotation about the orthogonal crystallographic x, y, and z axes, respectively. Thus, R_z is rotation about the film normal, and is analogous to the azimuthal angle when either R_x or R_y is negligible.

C. Example

The system chosen for these initial calculations is a monolayer composed of stearic acid amphiphiles in the conformation found in form C^{15} . The calculation of the one molecule per unit cell most clearly illustrates this method. The calculated minimum energy (Table I) is determined with respect to all degrees of freedom for an ordered lattice. A quasihexagonal (planar group p6m, point group C_{6v}) reference state may then be defined by appropriately distorting the lattice according to Eq. (3) above. This symmetry can apply to the reported high-pressure, high-temperature LS phase if one considers a vertical molecule averaged over all orientations about the film normal.¹⁰ In a system of p6msymmetry, ε_1 is totally symmetric and ε_2 and ε_6 transform according to the irreducible representation E_2 . The energy $V(\Omega^*(\varepsilon))$ is then identical with respect to a scan over either ε_2 or ε_6 , since these orthogonal variables couple bilinearly with appropriate orthogonal spherical harmonics of identical E_2 symmetry.¹⁰ Fatty acids in an ordered phase, however, are never higher symmetry than C_{σ} , which leads to planar groups of lower symmetry. In general this necessitates consideration of a complete set of states including both ε_6 and ε_2 , as well as ε_1 . In practice it was found that the lowest energy states for this system accompanied changes in ε_6 , and so this variable was studied in detail with ε_2 set to 0. If this reduced set contains the lowest energy states and the lowest energy path between them, it will give a good first order prediction of the phase behavior of this system, as well as being less complicated to interpret and much more efficient to calculate. The effect of ε_1 is included in the minimization of the area, which in practice changes only slightly along the minimum energy path.

By scanning the shear strain ε_6 over all states while minimizing the energy with respect to the orientational degrees of freedom and ε_1 , the results in Fig. 1 were obtained. There is a sudden change in the tilt angle R_y at shear strain ≈ 0.19 , from 0 to 14.69° (Fig. 2). Because R_x is nearly 0 for the entire set of states scanned (Fig. 3), R_y corresponds to the tilt angle and R_z to the azimuthal angle (Fig. 4). This allows the separation of phase space into two and the definition of a vertical and a tilted phase, with the magnitude of the tilt angle R_y fixed at 0 and 14.69°, respectively. The remaining energies for these two defined phases were then calculated, and complete curves are shown in Fig. 1.

The curves in Fig. 1 were fit to a 16th order polynomial



FIG. 1. Strain-state curves for vertical and tilted phases, 1 molecule/unit cell, plotting energy versus shear strain, ε_6 . The vertical and tilted phase curves are found by fixing the tilt magnitude to 0 and 14.69°, respectively. The lower curve at every point is found when minimizing with respect to all degrees of freedom.



FIG. 2. Tilt angle R_y versus shear strain, ε_6 . The average magnitude of the two nonzero portions of the plot defines the tilted phase geometry.

by a chi-square minimization. This was then used to calculate the strain-state partition function as the integral

$$Q^{\varepsilon} = \int_{\text{period}} \exp(-\beta V(\Omega^*(\varepsilon))) d\varepsilon.$$

Since the pure shear strain ε_6 results in a periodic function (Fig. 1), the integral is performed over one period. These functions are sufficiently simple that they may be integrated using Romberg integration.¹⁸ These curves show that the shear elastic constant c_{66} is negative for the reference hexagonal system, and therefore obviously the hexagonal phase is unstable with respect to shear strain due to the coupling with the orientational fluctuations. In other words, since the alkane chain has no more than C_{σ} symmetry, it cannot be accommodated in an ordered phase by a C_{6v} translational subsystem. Furthermore, any translational–rotational coupling will lead to a breaking of C_{6v} symmetry.



FIG. 4. Azimuthal angle R_z versus shear strain, ε_6 . This plot is considerably more linear than that of R_x and R_y .

IV. RESULTS

The one molecule unit cell results have been introduced above. Surprisingly, tilting behavior is quite discontinuous with respect to shear strain, indicating nonlinear coupling between the tilt angle R_y and ε_6 (see Fig. 2). Since there are two phases found with respect to a scan of ε_6 , vertical and tilted, these were treated separately to determine the ground state and possible transitions. There is considerably more linear coupling between R_z (the azimuthal angle) and ε_6 , as shown in Fig. 4. This coupling results in the continuum of states shown in Fig. 1.

Free energy contributions were calculated as described above. Calculations including no numerically applied pressure indicate the stable phase at all temperatures is the vertical phase (Fig. 5). A negative surface pressure must be introduced to produce a tilted phase. This rescaling is attributed to the effect of head group and surface interactions, which can cause the film to expand.¹⁹ The magnitude of the surface pressure difference applied here is similar to that



FIG. 3. Tilt angle R_x versus shear strain, ε_6 . Note the small magnitude of this angle.



FIG. 5. Strain-state free energy contributions for vertical and tilted phases (1 molecule/unit cell) at 0 applied surface pressure.

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FIG. 6. Strain-state free energy contributions for vertical and tilted phases (1 molecule/unit cell) at an applied surface pressure of -50. The sign of this pressure is attributed to a rescaling due to surface and head group interactions.

required to produce a vertical phase on the aqueous surface. Estimates of the transition temperature were calculated as shown in Fig. <u>6</u>, indicating a transition from a vertical to a tilted phase with increasing temperature.²⁰ Though this transition temperature is unobtainable in practice, it increases with decreasing applied pressure.

The calculated minimum for a two-molecule unit cell (as proposed for the CS phase $\frac{1.8}{1.8}$ is essentially identical in energy to that found for a one-molecule unit cell (Table I, Figs. 7 and 8). Two phases are again found upon scanning ε_6 , a vertical herring-bone phase of symmetry pg, and a tilted phase of symmetry pm. The herring-bone pg phase contains a crystallographic glide plane between the molecules, while in the tilted pm phase this is replaced by a mirror plane coincident with the mirror plane along the fatty acid chain. A twofold axis is found between the tilted molecules and parallel to their long axis, but not coincident with a crystallographic axis. The long axes of these molecules are therefore parallel, but the rotation about these long axes differs by 180 degrees. This phase is therefore denoted as the antiparallel phase. A third phase of higher energy is also found which exhibits a crystallographic twofold axis between pairs of molecules of significant tilt magnitude. This nonuniformly



FIG. 7. Projection of the vertical phase (1 molecule/unit cell).



FIG. 8. Projection of the herring bone (pg) phase (2 molecules/unit cell).

tilted *pm* phase was not investigated in detail. The antiparallel *pm* phase is extremely similar to the original tilted phase of one molecule per unit cell (Figs. 9 and 10), as is clearly demonstrated by viewing these phases down the long axes of the molecules. The closest distance between molecular centers in the plane perpendicular to the long molecular axis is 4.11 and 4.14 Å for the tilted and antiparallel phases, respectively. The corresponding tilt angles are 74.2 and 76.6°. Since reorienting a given molecule in these two phases by 180° with respect to its surrounding molecules makes little energetic difference, it seems highly unlikely that such phases will exhibit long coherence lengths in the condensed phase.

The results from two-molecule per unit cell systems are shown in Fig. 11. A clear transition between the pg herring-



FIG. 9. Perspective projection along the long axis of the molecule of the tilted phase (1 molecule/unit cell).



FIG. 10. Perspective projection along the long axis of the molecule of the tilted antiparallel (pm) phase (2 molecules/unit cell). The orientation of the molecules depicted in the center row is rotated 180° about the long axis.

bone and the *pm* tilted antiparallel phase is found with increasing temperature. This may be compared to a *CS-S'* transition.¹ The slopes of these curves are considerably different at the crossing point. This indicates a high entropy of transition (\sim 3 cal/mol·K) and therefore a first order transition, in agreement with phase-coexistence reports in the literature.⁸

V. CONCLUSIONS

These calculations should be viewed as an attempt to model Langmuir monolayers by a realistic potential while exploiting the underlying order and symmetry of these systems to arrive at reasonable predictions of the most likely phases. It is intended to illustrate the feasibility of such an approach, and should include several extensions for quantitative agreement with experiment. These include a more detailed description of the interaction of the head groups with the substrate, especially their chemical nature and their relation to the surface pressure. Orientational disorder about the tail axis, as well as conformational disorder, should also be modeled.^{21,22} As such, conclusions from this work must still be expressed qualitatively, although they arise from potentials that are considered to be reasonably realistic.

One-molecule per unit cell results are illustrative and clear, but are not directly comparable to most π -*T* phase diagrams, which describe ordered condensed phase unit cells as containing two molecules. Nonetheless, the high surface pressure calculations predict no transition between vertical and tilted phases with respect to temperature, and the qualitatively necessary result of tilt with decreasing surface pres-



FIG. 11. Strain-state free energy contributions for herring bone (pg) and tilted antiparallel (pm) phases (2 molecules/unit cell) at 0 applied surface pressure.

sure is obtained. Further data are necessary to determine the slope of the line separating vertical and tilted phases at intermediate pressures. There is nonlinear coupling between the tilt magnitude and the shear strain (Fig. 2), but a much more linear coupling with what in practice is the azimuthal angle of the amphiphile (Fig. 4). The graph of $V(\Omega^*(\varepsilon))$ in Fig. 1 allows for the straightforward determination of the shear elastic constant c_{66} by this methodology. It also may facilitate the calculation of coupling constants involving ε_6 and orientational variables (Ω_i) in the Landau free energy expansion. By sequentially setting ε_i and then Ω_i to zero, and performing further scans involving the remaining variables, one may quantitatively obtain all the constants in the Landau expansion.

Two-molecule per unit cell systems exhibit a tilting transition with respect to temperature, and the considerable divergence of the two free energy contribution curves indicates it is a first order transition. This may be compared with recently reported coexistence of similar phases.⁸ Certainly details of the potential are important, since the potential energy surface is in general quite flat, with many close lying local minima. This can lead to metastable states, or polyamorphism,²³ which will be the subject of future work.

The curves in Fig. 1 lend a unique view of fatty acid monolayers. These results indicate that at low temperatures the monolayer is ferroelastic, as predicted.¹⁰ Stress is caused by orientational fluctuations, although these calculations derive this necessary stress by first fixing the strain. Clearly, a tilted amphiphile introduces an elastic dipole, which is a local stress, into the system.²⁴ Domains, represented by the minima in the double-well potential, decrease in size with increasing temperature until finally a phase that has average hexagonal symmetry results. This mesophase is reached when the barrier between the minima is overcome, although there remains a higher barrier to larger shear strain. At high enough temperature, this barrier is also overcome, and a truly liquid state is obtained. Aside from this qualitative picture, this investigation of stress–strain relationships has repro-

duced several features of the fatty acid phase diagram. Extensions to include the chemical nature of the head groups, the disorder of the tail groups, and the explicit contributions of the other strain variables will further improve the quantitative predictions of these preliminary calculations.

This methodology may prove even better suited to inclusion compounds such as alkane derivatives in urea, which have been analyzed in this context.^{25,26} Here, neglecting interalkane translational contributions may be justified, and the explicit calculation of contributions from the urea cage are not complicated by solvent interactions, as in the case of head groups considered here. This makes calculation of $V^T(\{\varepsilon\})$ straightforward. The remaining parts of the energy are similarly accessible computationally.

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