

# The Effect of Gauche Molecular Conformations on the Phase Diagram of a Langmuir Monolayer

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Experimental and simulation studies have shown that the gauche conformational degrees of freedom of long-chain amphiphile molecules assembled in a dense Langmuir monolayer play an important role in determining the structures of the several phases that the monolayer supports. Nevertheless, for simplicity the extant theoretical analyses of the Langmuir monolayer phase diagram ignore gauche molecular conformations, thereby treating the amphiphile molecules as rigid rods. We propose a description of the influence of the conformational degrees of freedom of a long-chain amphiphile molecule on the phase diagram of a Langmuir monolayer. Our analysis extends the Landau-type theory of the Langmuir monolayer diagram formulated by Kaganer and Loginov (*Phys. Rev. E* **1995**, *51*, 2237–2249). The gauche defects are represented by a secondary order parameter coupled to the Kaganer–Loginov primary order parameters (the tilt vector of the molecules and the density waves describing herringbone ordering along and normal to the line of centers between molecules). The effect of the gauche conformations is to modify the coefficients of the primary order parameters in the free energy expansion and thereby to change the location of the transition lines in the phase diagram. For transitions that are induced by a change in the surface pressure, the tilting transitions, we obtain a shift of the transition lines to lower surface pressure. For transitions that are induced by lowering the temperature, the crystallization transitions, we suggest, given some restrictions on the magnitude of the coefficients of the coupling terms, that the transition lines shift to lower temperature.

## I. Introduction

Although Langmuir monolayers of long-chain amphiphile molecules supported at the air–water interface have been studied for the greater part of a century,<sup>1,2</sup> it is only in the last 2 decades that experimental determinations of the molecular packing as a function of surface coverage have been reported.<sup>3–10</sup> These studies, mostly based on grazing incidence X-ray diffraction experiments, supplement older studies of the dependence of surface pressure on area per molecule, and contemporary studies that exploit Brewster angle microscopy and polarization fluorescence microscopy of the monolayer as a function of surface coverage.<sup>11–22</sup> Taken together, the results obtained reveal a remarkably rich phase diagram in the high surface

density regime of the Langmuir monolayer. The interpretation of that phase diagram depends on two important theoretical developments and an assumption concerning the internal conformation of the amphiphile molecule. The first theoretical development, the Kosterlitz–Thouless–Halperin–Nelson–Young (KTHNY) theory of melting in a two-dimensional system, predicts the existence of a new and unusual phase between the two-dimensional liquid and ordered solid phases, the so-called hexatic phase.<sup>23–27</sup> The second theoretical development, the Kaganer–Loginov (KL) description of the overall topology

- (1) Langmuir, I. *J. Chem. Phys.* **1933**, *1*, 756–776.
- (2) Stenhagen, E. In *Determination of Organic Structures by Physical Methods*, Braude, E. A., Nachod, F. C., Eds.; Academic Press Inc.: New York, 1955; Vol. 1, pp 325–371.
- (3) Bibo, A. M.; Knobler, C. M.; Peterson, I. R. *J. Phys. Chem.* **1991**, *95*, 5591–5599.
- (4) Knobler, C. M.; Desai, R. C. *Annu. Rev. Phys. Chem.* **1992**, *43*, 207–236.
- (5) Riviere, S.; Henon, S.; Meunier, J.; Schwartz, D. K.; Tsao, M. W.; Knobler, C. M. *J. Chem. Phys.* **1994**, *101*, 10045–10051.
- (6) Lawrie, G. A.; Barnes, G. T. *J. Colloid Interface Sci.* **1994**, *162*, 36–44.
- (7) Fischer, B.; Teer, E.; Knobler, C. M. *J. Chem. Phys.* **1995**, *103*, 2365–2368.
- (8) Durbin, M. K.; Malik, A.; Richter, A. G.; Ghaskadvi, R.; Gog, T.; Dutta, P. *J. Chem. Phys.* **1997**, *106*, 8216–8220.
- (9) Lautz, C.; Fischer, T. M. *J. Phys. Chem. B* **1997**, *101*, 8790–8793.
- (10) Kaganer, V. M.; Möhwald, H.; Dutta, P. *Rev. Mod. Phys.* **1999**, *71*, 779–819.
- (11) Kjaer, K.; Als-Nielsen, J.; Helm, C. A.; Laxhuber, L. A.; Möhwald, H. *Phys. Rev. Lett.* **1987**, *58*, 2224–2227.

- (12) Dutta, P.; Peng, J. B.; Lin, B.; Ketterson, J. B.; Prakash, M.; Georgopoulos, P.; Ehrlich, S. *Phys. Rev. Lett.* **1987**, *58*, 2228–2231.
- (13) Lösche, M.; Möhwald, H. *Rev. Sci. Instrum.* **1984**, *55*, 1968–1972.
- (14) Moy, V. T.; Keller, D. J.; Gaub, H. E.; McConnell, H. M. *J. Phys. Chem.* **1986**, *90*, 3198–3202.
- (15) Henon, S.; Meunier, J. *Rev. Sci. Instrum.* **1991**, *62*, 936–939.
- (16) Hönig, D.; Möbius, D. *J. Phys. Chem.* **1991**, *95*, 4590–4592.
- (17) Overbeck, G. A.; Möbius, D. *J. Phys. Chem.* **1993**, *97*, 7999–8004.
- (18) Schwartz, D. K.; Knobler, C. M. *J. Phys. Chem.* **1993**, *97*, 8849–8851.
- (19) Durbin, M. K.; Malik, A.; Ghaskadvi, R.; Shih, M. C.; Zschack, P.; Dutta, P. *J. Phys. Chem.* **1994**, *98*, 1753–1755.
- (20) Kaganer, V. M.; Peterson, I. R.; Kenn, R. M.; Shin, M. C.; Durbin, M.; Dutta, P. *J. Chem. Phys.* **1995**, *102*, 9412–9422.
- (21) Kuzmenko, I.; Kaganer, V. M.; Leiserowitz, L. *Langmuir* **1998**, *14*, 3882–3888.
- (22) Kaganer, V. M.; Brezesinski, G.; Möhwald, H.; Howes, P. B.; Kjaer, K. *Phys. Rev. E* **1999**, *59*, 2141–2152.
- (23) Kosterlitz, J. M.; Thouless, D. J. *J. Phys. C* **1972**, *5*, L124–L126.
- (24) Kosterlitz, J. M.; Thouless, D. J. *J. Phys. C* **1973**, *6*, 1181–1203.
- (25) Halperin, B. I.; Nelson, D. R. *Phys. Rev. Lett.* **1978**, *41*, 121–124.
- (26) Nelson, D. R.; Halperin, B. I. *Phys. Rev. B* **1979**, *19*, 2457–2484.
- (27) Young, A. P. *Phys. Rev. B* **1979**, *19*, 1855–1866.

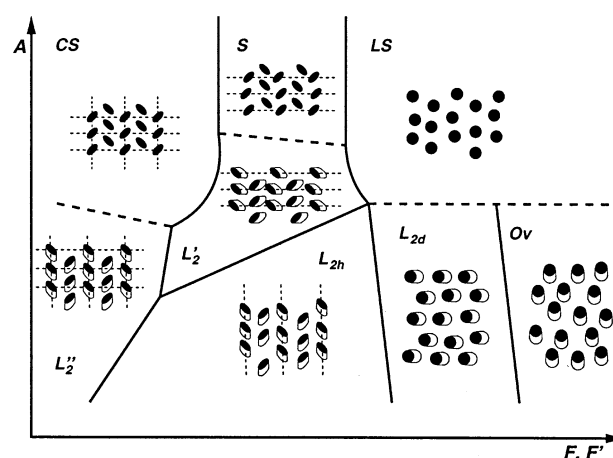
of the phase diagram, is based on a Landau theory analysis of a two-dimensional free energy functional with three-order parameters.<sup>28,29</sup> This theory successfully predicts the observed phase transitions as successive orderings of the hexatic phase.

One of the order parameters used by Kaganer and Loginov describes the collective tilt of the amphiphile molecules. The other two-order parameters describe weak one-dimensional crystallization involving herringbone ordering of the all-trans carbon skeletons of the amphiphile molecules along the line between nearest neighbors and the normal to it. The important assumption concerning the internal conformation of the amphiphile molecule is that it is in the all-trans state. Neither the KTHNY nor the KL analyses include the contribution of molecular gauche conformations to the free energy and, hence, ignore the possible influence of those molecular conformations on the phase diagram of the monolayer.

A few more words are appropriate with regard to the neglect of gauche conformations of the amphiphile molecules in the KL analysis, because it is sometimes stated that their analysis implicitly contains the actual density of those conformations. This point of view is based on the assertion that the order parameter associated with the gauche conformations is not singular at the phase transition point; hence minimization of the free energy with respect to that order parameter only leads a renormalization of the coefficients in the Landau free energy expansion that has the effect of generating an uninteresting shift of the phase transition line. The shift of the phase transition line is said to be uninteresting because the values of the coefficients in the Landau theory expansion of the free energy before the renormalization are not known, and only the renormalized values can be measured. However, it is a fact that some amphiphile molecules have gauche conformations in some regions of the phase diagram while others do not; i.e., the identity of the amphiphile molecule matters. It is also a fact that the concentration of gauche conformations is not constant across the phase diagram. Then representation of the differences between the phase diagrams of different systems and of the role of internal molecular conformations on a particular phase diagram requires, at a minimum, an additional order parameter, for which we select the gauche conformation concentration. Setting the coefficients of the gauche conformation concentration in the Landau free energy expansion equal to zero indeed regenerates the original KL form of that expansion. But without the gauche conformation order parameter there can be no discussion of trends in the evolution of the monolayer structure that occur when gauche conformations are present, e.g., the positions of the phase transition lines as a function of gauche conformation concentration.

## II. Background Information

An amphiphile molecule consists of two parts, a hydrophilic headgroup and a hydrophobic hydrocarbon tail (typically a saturated alkane chain). In the condensed monolayer phases of these molecules, the hydrophilic headgroup is in contact with the water surface while the



**Figure 1.** A generic phase diagram for amphiphilic molecules at the air/water interface reproduced from ref 29. The  $F$  and  $F'$  parameters that define the  $x$ -axis are temperature-like variables and the  $A$  parameter that defines the  $y$ -axis is a surface-pressure-like variable. Solid lines represent first-order phase transitions while dashed lines represent second-order phase transitions. Reprinted with permission from ref 29. Copyright 1995 American Physical Society.

hydrophobic hydrocarbon tail points away from the water surface. In the KL theory, the complex polymorphism of the phase diagram is a consequence of the coupling between inter- and intramolecular degrees of freedom of rigid all-trans amphiphile molecules. However, it is plausible that the neglected internal conformation degrees of freedom of the hydrocarbon tail of the amphiphile molecule will also influence the location of phase boundaries.

The many phases in the high-density region of the Langmuir monolayer phase diagram are conveniently classified in two groups. In the first group, at high temperature, are the mesophases. The molecules in these phases are arranged in locally hexagonal or distorted hexagonal (centered rectangular) lattices with quasi-long-range orientation order and short-range translational order. In the second group are the crystalline phases characterized by both long-range orientation and translational order. The intramolecular degrees of freedom used to characterize the amphiphile molecules are the tilts of the long axes, the ordering of the backbone plane (short axes or herringbone ordering), and the dihedral angle conformations along the hydrocarbon tail of the molecule.

A large number of experimental studies of Langmuir monolayer structure have been concerned with fatty acid molecules. It has been shown that monolayers of these amphiphiles satisfy a version of corresponding states behavior. That is, it is possible to superpose the phase transition lines of monolayers of fatty acids with different hydrocarbon chain lengths and thereby generate a (universal) generic phase diagram. This is accomplished by shifting the temperature axis by about 5 °C for each additional methylene group in the amphiphile molecule.<sup>30,31</sup> This generic phase diagram is displayed in Figure 1. The shapes of the unit cells in the different phases, determined by X-ray diffraction, are also shown in Figure 1. The CS and S phases are crystalline, while LS,  $L_2'$ ,  $L_2''$ ,  $L_{2h}$ ,  $L_{2d}$ , and Ov are the mesophases. There are five tilted phases with distinct symmetries. Phases  $L_2$  and  $L_2''$  have a collective tilt of the molecules toward one

(28) Kaganer, V. M.; Loginov, E. B. *Phys. Rev. Lett.* **1993**, *71*, 2599–2602.

(29) Kaganer, V. M.; Loginov, E. B. *Phys. Rev. E* **1995**, *51*, 2237–2249.

(30) Bibo, A. M.; Peterson, I. R. *Adv. Mater.* **1990**, *2*, 309–311.

(31) Peterson, I. R.; Brzezinski, V.; Kenn, R. M.; Steitz, R. *Langmuir* **1992**, *8*, 2995–3002.

of their nearest neighbor (NN) molecules, whereas in  $L_2'$  and  $O_v$  the collective tilt is toward the next nearest neighbor (NNN). Some aspects of the phase diagram remain unresolved, specifically, the order of the transition lines and the existence of additional phases at very high surface pressure.

The KL theory is a symmetry-based description of phase transitions in a Langmuir monolayer that is set in the framework of the Landau theory of phase transitions.<sup>32,33</sup> The treatment is based on a Taylor series expansion of the free energy in powers of one or more order parameters. The order parameters form a set of scalar quantities that represent the structural changes across the transition lines. Each order parameter is constructed such that on one side of the transition line it is zero while on the other side it is nonzero. The behavior of an order parameter under symmetry transformations that belong to the symmetry group representing the most symmetric phase is described by one of the irreducible representations of that group. This irreducible representation and the condition that the free energy is invariant and homogeneous under the action of any symmetry element determine the polynomial form of the order parameter.

The starting point in any Landau theory description of the character of phase transitions is the identification of the symmetries of the phases under study. The overall scheme of analysis starts with the least ordered condensed phase of the monolayer and examines the progressive increase in ordering as different order parameters assume nonzero values. It is assumed that the relative positions of the molecules in the two phases under consideration differ only slightly. Several phenomenological approaches based on Landau theory have been formulated to describe the phase diagram of a Langmuir monolayer.<sup>34–38</sup> The main difference between these approaches is in the identification of the order parameters that change in the various transitions. In the KL treatment<sup>28,29</sup> the most symmetric phase is the LS phase; it is assigned to the  $C_{6v}$  point group. All other phases emerge as a result of successive ordering of three-order parameters. One-order parameter governs the collective tilt of the molecules while the other two describe one-dimensional “weak crystallization”<sup>39</sup> involving herringbone ordering of the short axes of the amphiphile molecule along and normal to the line between neighboring molecules (the “bond” direction). The free energy expansion in powers of the order parameters includes only the lowest order terms that are necessary to describe the transition. The coefficients of the lowest order of each order parameter are functions of surface pressure and temperature. By use of information derived from the experimental phase diagrams, a collective tilt of the molecules is induced by lowering the surface-pressure-like variable ( $A$  in Figure 1). Similarly, the herringbone ordering of the backbone planes of the molecules is induced by decreasing the values of the temperature-like variables ( $F, F'$  in Figure 1). All other coefficients are considered to be constant. Their signs and magnitudes are determined by the requirements that the phase be stable and that the

observed transition order and structural symmetries be reproduced. Different combinations of the three-order parameters generate a phase diagram with eight phases with different symmetries. The KL treatment considers the molecules to be rigid rods, with no internal degrees of freedom. This assumption is valid for the lowest energy all-trans conformation of the hydrocarbon chain, which is expected to be the only one present in the low temperature, high-pressure region of the phase diagram. However, as the area per molecule increases gauche conformations of the hydrocarbon chain are expected to be populated because of the higher chain entropy thereby generated.

Quantities associated with conformational degrees of freedom of the amphiphile molecules assembled in a monolayer are very difficult to measure. Buontempo and Rice and Li and Rice showed that it is possible to use the difference between the frequencies of the antisymmetric and symmetric stretching modes of  $CH_2$  in a hydrocarbon chain, measured via polarized infrared reflection spectroscopy, to calculate the concentration of gauche conformations. Their studies showed that the isotherms of Langmuir monolayers of heneicosanol, stearyl alcohol, and tetracosanoic acid reveal a clear trend of continuous transition from a phase with intramolecular chain disorder to one with intramolecular chain order.<sup>40–42</sup> At high surface pressure and low temperature, the hydrocarbon chains are highly ordered (perhaps all-trans), whereas at low surface pressure and high temperature the hydrocarbon chains become disordered and contain a nontrivial concentration of gauche defects. X-ray diffraction studies of fluorinated alkyl acid monolayers reveal that they have different ordered phases than do fully hydrogenated acid monolayers, presumably as a result of the difference in chain flexibility.<sup>43</sup>

The ability of an amphiphile molecule to support gauche defects depends on the stiffness of the hydrocarbon chain and on its length. Gauche defects are classified into three categories. In the first category are isolated defects which appear in bonds 2, 3,  $n - 2$ ,  $n - 1$  (where the headgroup  $C_1$  bond is numbered 0); these are called “end gauche defects”. In the second category are the “kink defects” formed by a pair of gauche defects separated by a trans bond. The third category represents isolated defects in the middle of the chain. Molecular dynamics simulations show that upon isothermal expansion a Langmuir monolayer undergoes two phase transitions.<sup>44–46</sup> The first is a continuous transition from an all-trans state of the hydrocarbon tails to chains that include a high fraction of gauche defects with no change in the lattice order. The second transition is a discontinuous melting transition from a triangular lattice state to a liquidlike state. A mean field statistical model of short alcohol monolayers found that the average number of gauche defects is a function of the area per molecule saturates.<sup>47</sup> The average saturation concentrations of the defects were found to be 1.8/molecule and 4.2/molecule for the shortest ( $C_6$ ) and the longest ( $C_{16}$ ) chains studied. When the area per molecule

(32) Landau, L.; Lifshitz, E. *Statistical Physics*; Pergamon Press: Oxford, 1986.

(33) Tolédano, J.-C.; Tolédano, P. *The Landau Theory of Phase Transitions*; World Scientific: Singapore, 1987.

(34) Selinger, J. V.; Nelson, D. R. *Phys. Rev. Lett.* **1988**, *61*, 416–419.

(35) Selinger, J. V.; Nelson, D. R. *Phys. Rev. A* **1989**, *39*, 3135–3147.

(36) Luty, T.; Eckhardt, C. J. *J. Phys. Chem.* **1995**, *99*, 8872–8887.

(37) Mukherjee, P. K.; Deutsch, M. *Phys. Rev. B* **1999**, *60*, 3154–3162.

(38) Luty, T.; Swanson, D. R.; Eckhardt, C. J. *J. Chem. Phys.* **1999**, *110*, 2606–2611.

(39) Kats, E. I.; Lebedev, V. V.; Muratov, A. R. *Phys. Rep.* **1993**, *228*, 1–91.

(40) Buontempo, J. T.; Rice, S. A. *J. Chem. Phys.* **1993**, *98*, 5835–5846.

(41) Buontempo, J. T.; Rice, S. A. *J. Chem. Phys.* **1993**, *99*, 7030–7037.

(42) Li, M.; Rice, S. A. *J. Chem. Phys.* **1996**, *104*, 6860–6876.

(43) Barton, S. W.; Goudot, A.; Bouloussa, O.; Rondelez, F.; Lin, B.; Novak, F.; Acero, A.; Rice, S. A. *J. Chem. Phys.* **1992**, *96*, 1343–1351.

(44) Karaborni, S.; Toxvaerd, S. *J. Chem. Phys.* **1992**, *96*, 5505–5515.

(45) Karaborni, S.; Toxvaerd, S.; Olsen, O. H. *J. Phys. Chem.* **1992**, *96*, 4965–4973.

(46) Karaborni, S. *Langmuir* **1993**, *9*, 1334–1343.

(47) Rieu, J. P.; Vallade, M. *J. Chem. Phys.* **1996**, *104*, 7729–7740.

is small, the “end gauche defects” are most probable. When the area per molecule increases, isolated defects in the middle of the chain and/or “kink defects” have the highest probability of occurrence.<sup>44,48,49</sup> Nonequilibrium experimental and computational studies reveal a strong correlation between the gauche defects and the tilt angle of the molecules.<sup>50</sup> Moreover, the relaxation time of the internal chain conformation was found to be longer than that for the tilt transition. Karaborni and Verbist showed that when the area per molecule is fixed, an increase in the number of gauche defects results in a lower tilt angle.<sup>51</sup> Thus, the experimental and computational evidence available suggests that gauche defects should be coupled to the order parameters that describe the structural transitions in a Langmuir monolayer.

### III. An Extension of the Kaganer–Loginov Theory

The major features of the phase diagram of Langmuir monolayers are explained using the order parameters introduced by Kaganer and Loginov.<sup>29</sup> Therefore, extension of the analysis to include an order parameter that characterizes the gauche conformational degrees of freedom should not influence the possible symmetries of the various phases. An order parameter of this type is called “secondary”;<sup>33</sup> the original set of order parameters, the collective tilt and the herringbone ordering along two orthogonal axes, are termed “primary”. The gauche conformation order parameter should be nonzero above some critical temperature ( $T_c$ ) or below some critical surface pressure ( $\pi_c$ ). Furthermore, it should be coupled to transitions described by the primary order parameters. In this formalism the possible symmetries of the different phases are determined by the primary order parameters. However, restrictions on the possible symmetries of the irreducible representations that are carried by the secondary order parameter can be imposed depending on the order of the transitions. Because herringbone ordering is a first-order transition, there is no symmetry requirement imposed on the secondary order parameter. However, for a continuous transition, such as the tilt transition, a necessary condition for the gauche conformation order parameter to acquire a nonzero value above (in terms of surface pressure) the tilting transition is the possibility to construct from its components and that of the tilt order parameter a mixed homogeneous polynomial invariant under  $C_{6v}$ , that is linear in the gauche order parameter and of degree equal to or greater than 2 in the tilt order parameter.<sup>33</sup> Therefore, for a second-degree polynomial (the lowest degree polynomial of the tilt order parameter), we must decompose the symmetrized square of the  $E_1$  irreducible representation (representing the tilt vector). This process yields either  $A_1$  or  $E_2$  symmetry for the gauche conformation order parameter.

In the rotator phases of the monolayer, the molecular chains are free to rotate around their long axes; hence there is no directionality associated with the gauche defects. Further, we assume that in phases where the molecules are not free to rotate around their long axes the directionality of the gauche defects is not correlated with the symmetry of the phase, as can be inferred from simulation results that describe coupling between posi-

tional ordering and gauche defects.<sup>44,46</sup> Hence, we introduce this order parameter,  $\zeta$ , as a scalar ( $A_1$  symmetry) that is equal to the fraction of gauche conformations of the long chain molecules

$$\zeta = \langle N_g \rangle / N_d \quad (1)$$

where  $\langle N_g \rangle$  is the average number of gauche conformations and  $N_d$  is the total number of dihedral angles along the chain. The part of the free energy depending solely on  $\zeta$  is of the form

$$\Phi_\zeta = a\zeta + \frac{b}{2}\zeta^2 + \frac{c}{3}\zeta^3 + \dots \quad (2)$$

Terms of any degree in  $\zeta$  are allowed by symmetry to be present in  $\Phi_\zeta$ . Since  $\zeta = 0$  for the all-trans conformation and  $\zeta \neq 0$  when gauche conformations are present, the coefficient  $a = a(T, \pi)$  should be positive in the low-temperature (or high surface pressure) region and negative in the high-temperature (or low surface pressure) region, e.g.,  $a = \alpha(T_c - T)$ , with  $\alpha > 0$ . For stability it is necessary that  $b > 0$ .

Since any power of  $\zeta$  multiplied by any invariant polynomial of the primary order parameter will be invariant, the lowest degree coupling terms between the gauche conformation order parameter and the herringbone order parameters are products between the linear term in  $\zeta$  and the lowest allowed polynomial of these primary order parameters. The lowest degree coupling term with the tilt order parameter is also linear but it is obtained via a symmetry condition on the coupling to a continuous transition. Minimization of the coupled free energy expansion with respect to  $\zeta$  gives the equilibrium value of  $\zeta$  as a function of the primary order parameter. With this relation we can eliminate  $\zeta$  in the expression for the free energy. Therefore, the effect of introducing the gauche conformation order parameter is to modify the coefficients of the free energy expansion associated with the primary order parameters. Of course, the coefficients in the free energy expansion determine the location of the transition lines. Thus, the effect of adding the gauche conformation order parameter coupling is to shift the transition lines in the phase diagram; the signs and the magnitudes of the coefficients of the primary and secondary-order parameters determine the direction of the shift. It is very likely that gauche conformations are present on both sides of the transition line in the high-temperature low surface pressure region. The exact location of the onset of gauche defects in the phase diagram depends on molecular properties such as stiffness (barriers to internal rotation) and amphiphile chain length.

**1. Coupling of the Internal Conformation and Tilt Order Parameters.** The tilting transition is represented by a 2D order parameter with the  $E_1$  symmetry of the  $C_{6v}$  point group. Let  $\beta$  be the azimuthal angle of the collective tilt (in the plane of the monolayer) and let  $\eta = \sin \theta$ , where  $\theta$  is the tilt angle with respect to the normal to the monolayer. The expansion of the free energy, invariant with respect to the symmetry group  $C_{6v}$ , is

$$\Phi_\eta = A\eta^2 + B\eta^4 - D\eta^6 \cos(6\beta) + E\eta^{12} \cos(12\beta) + \dots \quad (3)$$

**A. The  $LS \leftrightarrow O_v$  and  $LS \leftrightarrow L_{2d}$  Transitions.** The free energy expansion that is sufficient to describe this second-order transition includes only the first two terms in eq 3. When  $A > 0$ , the untilted phase case is obtained when

(48) Shin, S.; Collazo, N.; Rice, S. A. *J. Chem. Phys.* **1992**, *96*, 1352–1366.

(49) Shin, S.; Rice, S. A. *Langmuir* **1994**, *10*, 262–266.

(50) Buontempo, J. T.; Rice, S. A.; Karaborni, S.; Siepmann, J. I. *Langmuir* **1993**, *9*, 1604–1607.

(51) Karaborni, S.; Verbist, G. *Europhys. Lett.* **1994**, *27*, 467–472.

$\eta = 0$ . When  $A < 0$ , the nonzero tilt is determined by  $\eta_{\text{equil}}^2 = -A/2B$ . The transition line is then  $A = 0$ . The coefficient  $B$  is considered to be constant across the transition line. The condition of thermodynamic stability then requires that  $B > 0$ . The expansion of the free energy including the coupling to the gauche conformation order parameter is

$$\Phi_{\eta\zeta} = A\eta^2 + B\eta^4 + a\zeta + \frac{b}{2}\zeta^2 + \delta\zeta\eta^2 \quad (4)$$

from which we find

$$\zeta_{\text{equil}} = -\frac{a + \delta\eta^2}{b} \quad (5)$$

Elimination of  $\zeta$  in the free energy expansion yields

$$\Phi_{\eta, \zeta=\zeta_{\text{equil}}} = -\frac{a^2}{2b} + \left[A - \frac{a\delta}{b}\right]\eta^2 + \left[B - \frac{\delta^2}{2b}\right]\eta^4 \quad (6)$$

The term  $-a^2/2b$  changes only the background value of the free energy, so the new transition line is defined by  $A = a\delta/b$ . Since both the gauche conformations and the tilt angle increase as the area per molecule increases, the coupling between the two-order parameters should contribute a positive term to the free energy. We conclude that  $\delta > 0$ . Since  $a < 0$ , the new transition line shifts to lower surface pressure. The new equilibrium value of the tilt in the presence of gauche conformations is

$$\eta_{\zeta, \text{equil}}^2 = -\frac{A - a\delta/b}{2(B - \delta^2/2b)} \quad (7)$$

However, without information regarding the magnitude of the primary and secondary coefficients, it is not possible to determine whether the collective tilt increases or decreases. Nevertheless, molecular dynamics simulations indicate that the collective tilt decreases<sup>51</sup> which requires that  $a/A > \delta/2B$ .

**B. The  $O_v \leftrightarrow L_{2d}$  Transition.** The value of  $\beta$  changes across this transition from  $\beta = \pi/6$  corresponding to NNN tilt in the  $O_v$  phase, to  $\beta = 0$  corresponding to NN tilt in the  $L_{2d}$  phase. Hence, the expansion of the free energy in powers of the order parameters must include higher degree terms that depend on  $\beta$

$$\Phi_{\eta\beta\zeta} = A\eta^2 + B\eta^4 - D\eta^6 \cos(6\beta) + E\eta^{12} \cos(12\beta) + a\zeta + \frac{b}{2}\zeta^2 + \delta\zeta\eta^6 \cos(6\beta) \quad (8)$$

Substitution of  $\zeta_{\text{equil}} = -(a + \delta\eta^6 \cos(6\beta))/b$  for  $\zeta$  in eq 8 yields

$$\Phi_{\eta\beta, \zeta=\zeta_{\text{equil}}} = A\eta^2 + B\eta^4 - \left[D + \frac{a\delta}{b}\right]\eta^6 \cos(6\beta) + \left[E - \frac{\delta^2}{4b}\right]\eta^{12} \cos(12\beta) \quad (9)$$

The first-order transition line is described by the change of the sign of the coefficient of  $\eta^6 \cos(6\beta)$  from a negative value in the  $O_v$  phase to a positive value in the  $L_{2d}$  phase. The transition line is, therefore, given by  $D = -a\delta/b$ . Since  $\cos(6\beta)$  is negative in the phase with the larger area per molecule ( $O_v$ ), we take  $\delta < 0$  so that the coupling term makes a positive contribution to the free energy in that phase. This means that the amphiphilic molecules with gauche conformations favor tilt toward their nearest

neighbors ( $\beta = 0$ ) and the transition line shifts to a higher temperature relative to that when no gauche conformations are present ( $D = 0$ ). In passing we note that the direction of the  $D$  axis is opposite to the direction of the temperature-like axis shown in Figure 1. In the original treatment of Kaganer and Loginov, the coefficient of  $\eta^{12} \cos(12\beta)$ , namely  $E$ , is taken to be negative to ensure a first-order transition. In the present case, this condition,  $E < 0$ , is sufficient to guarantee that the modified coefficient,  $E - \delta^2/4b$ , is negative and that the transition is first order.

**2. Coupling of the Internal Conformation with the Herringbone Order Parameters.** When the monolayer has herringbone order, the orientation of the short axis of a particular amphiphile molecule is directed parallel to the line of centers ('bond') between molecules and orthogonal to the orientations of the short axes of its NN molecules. The transition from a phase with isotropic orientation of the backbone plane (rotator phase) to a phase with herringbone order is described by an order parameter that is analogous to the director of the long axis in a nematic phase. Furthermore, the center of mass positions of the molecules along or normal to the bond direction can be either ordered or disordered. This implies a translational ordering that can be considered to be a type of crystallization. A crystalline state is characterized by periodic spatial variations in the density. In the case under consideration, the transition to the new ordered state is assumed to obey the weak-crystallization approximation;<sup>39</sup> i.e., the discontinuity in the density is very small and the wave vectors of the relevant density variations have equal lengths. Then the density wave order parameter describing herringbone order must change sign upon reflection in the symmetry plane containing the wave vector. The mesophases  $S$ ,  $L_2'$ , and  $L_{2h}$  have a one-dimensional crystalline structure. Since long-range one-dimensional translational correlations are destroyed by thermal fluctuations,<sup>32,35</sup> these mesophases possess only short-range translational order. The phases  $CS$  and  $L_2''$  are two-dimensional crystals represented by two nonzero 1D density wave order parameters. Denoting the amplitude of the crystallization wave responsible for the ordering of the molecular backbone planes normal to the bond direction by  $\varphi$  and the one that induces the ordering parallel to the bond direction by  $\psi$ , the expansion of the free energy in terms of these order parameters takes the form

$$\Phi_{\varphi} = F\varphi^2 - G\varphi^4 + H\varphi^6 + \dots \quad (10)$$

$$\Phi_{\psi} = F'\psi^2 - G'\psi^4 + H'\psi^6 + \dots \quad (11)$$

respectively. The coefficients in eq 10 and eq 11 are taken to be positive to enforce the observed first-order transitions. On the high-temperature side of the transition, the minimum of the free energy occurs when  $\varphi = 0$  and  $\psi = 0$ . When a first-order transition occurs, a new phase with the same free energy per molecule (chemical potential) as the existing phase emerges. Then even when  $\varphi \neq 0$  and  $\psi \neq 0$ , we must have  $\Phi_{\varphi} = 0$  and  $\Phi_{\psi} = 0$ . The values of the order parameters are obtained, as usual, by minimizing the free energy. The minimization conditions allow the construction of a relation between the coefficients that describes the crystallization transition.

**A. The  $LS \leftrightarrow S$  and  $S \leftrightarrow CS$  Transitions.** The  $LS \leftrightarrow S$  transition is a one-dimensional crystallization of the short axes of the molecules in the monolayer. The part of

the free energy expansion that describes this transition with coupling to the gauche conformation order parameter is

$$\Phi_{\varphi\zeta} = F\varphi^2 - G\varphi^4 + H\varphi^6 + a\zeta + \frac{b}{2}\zeta^2 + \delta\zeta\varphi^2 \quad (12)$$

Using the equilibrium value of  $\zeta$ , namely,  $\zeta_{\text{equil}} = -(a + \delta\varphi^2)/b$ , the modified free energy expansion becomes

$$\Phi_{\varphi, \zeta=\zeta_{\text{equil}}} = \left[ F - \frac{a\delta}{b} \right] \varphi^2 - \left[ G + \frac{\delta^2}{2b} \right] \varphi^4 + H\varphi^6 \quad (13)$$

We note that  $\varphi^2$  changes from  $\varphi^2 = 0$  to  $\varphi^2 = (G + \delta^2/2b)/2H$  across the transition. A first-order transition occurs when the coefficient of  $\varphi^2$  decreases to  $(G + \delta^2/2b)^2/4H$ , so that the transition line changes to  $F = (G + \delta^2/2b)^2/4H + a\delta/b$ , whereas it has the form  $F = G^2/4H$  when gauche conformations of the amphiphile molecules are neglected. If  $\delta < 0$ , the transition line is shifted to higher temperature. If  $\delta > 0$ , the transition line is shifted to lower temperature provided that  $-a < \delta G/4H$ . The value of  $\varphi^2$  in the *S* phase coexisting with the *LS* phase (i.e., on the transition line) is larger when gauche conformations are present (in the rigid rods case  $\varphi^2 = G/2H$ ). This means that greater crystalline order is needed so that the free energies of both phases are equal.

The *S*  $\leftrightarrow$  *CS* transition is a 2D crystallization that occurs at a lower temperature than the *LS*  $\leftrightarrow$  *S* transition. It can be described by the order parameter  $\psi$  that is orthogonal to  $\varphi$ . The free energy expansion is the same as that in eq 12 with  $\varphi$  replaced by  $\psi$  and the coefficients  $F$ ,  $G$ , and  $H$  replaced by  $F'$ ,  $G'$ , and  $H'$ , respectively. Hence, the behavior of the transition line with respect to inclusion of coupling with gauche conformations is the same as for the *LS*  $\leftrightarrow$  *S* transition.

**B. The *S*  $\leftrightarrow$  *L*<sub>2</sub>' and *CS*  $\leftrightarrow$  *L*<sub>2</sub>'' Transitions.** The free energy expansion relevant to the analysis of the *S*  $\leftrightarrow$  *L*<sub>2</sub>' transition is

$$\Phi_{\eta\varphi\zeta} = A\eta^2 + B\eta^4 + I\varphi^2\eta^2 + J\varphi^2\eta^2 \cos(2\beta) + a\zeta + \frac{b}{2}\zeta^2 + \delta\zeta\eta^2 \quad (14)$$

Taking  $\beta = \pi/2$  for the NNN tilt in the *L*<sub>2</sub>' phase and minimizing  $\Phi_{\eta\varphi\zeta}$ , we obtain the new second-order transition line  $A = (J - I)\varphi^2 + a\delta/b$ . Since we are considering a tilting transition described by the order parameter  $\eta$ , we take  $\delta > 0$  as before. Then the modified transition line shifts to lower surface pressure relative to the line  $A = (J - I)\varphi^2$  that characterizes the transition when gauche conformations of the amphiphile molecule are neglected.

The *CS*  $\leftrightarrow$  *L*<sub>2</sub>'' transition also involves collective tilting of the amphiphile molecules; it is coupled to both  $\varphi$  and  $\psi$ . The free energy expansion relevant for the description of this transition is

$$\Phi_{\eta\varphi\zeta} = A\eta^2 + B\eta^4 + I\varphi^2\eta^2 + J\varphi^2\eta^2 \cos(2\beta) - I\psi^2\eta^2 - J\psi^2\eta^2 \cos(2\beta) + a\zeta + \frac{b}{2}\zeta^2 + \delta\zeta\eta^2 \quad (15)$$

Taking  $\beta = 0$  for the NN tilt in the *L*<sub>2</sub>'' phase and applying the same procedure as for the *S*  $\leftrightarrow$  *L*<sub>2</sub>' transition gives for the new transition line  $A = (J + I)\varphi^2 - (J + I)\psi^2 + a\delta/b$ . As in the preceding case, the transition line is shifted to lower surface pressure relative to the transition line  $A = (J + I)\varphi^2 - (J + I)\psi^2$  for the case when gauche conformations are neglected.

**C. The *L*<sub>2d</sub>  $\leftrightarrow$  *L*<sub>2h</sub> Transition.** The free energy expansion relevant to the analysis of the *L*<sub>2d</sub>  $\leftrightarrow$  *L*<sub>2h</sub> transition is

$$\Phi_{\psi\eta\zeta} = [F' - (J' \cos(2\beta) + I')\eta^2]\psi^2 - G'\psi^4 + H'\psi^6 + a\zeta + \frac{b}{2}\zeta^2 + \delta\zeta\psi^2 \quad (16)$$

In both phases the collective molecular tilt is toward the nearest neighbor so  $\beta = 0$ . Solving for the equilibrium value of  $\zeta$  followed by substitution of that value in the expression for the free energy yields

$$\Phi_{\psi\eta, \zeta=\zeta_{\text{equil}}} = \frac{a^2}{2b} + \left[ F' - (J' + I')\eta^2 - (a + \delta)\frac{a}{b} \right] \psi^2 - \left[ G' - \frac{\delta^2}{2b} \right] \psi^4 + H'\psi^6 \quad (17)$$

As  $F'$  decreases to the value  $(G' - \delta^2/2b)^2/4H' + (J' + I')\eta^2 + (a + \delta)a/b$ , a first-order transition occurs in which  $\psi$  changes from  $\psi^2 = 0$  to  $\psi^2 = (G' - \delta^2/2b)/2H'$ . If there are no gauche conformations in the molecule, the transition line is  $F' = G'/4H' + (J' + I')\eta^2$ . Thus, when  $\delta < 0$  the transition line shifts to higher temperature if  $a(a + \delta) > G'\delta^2/4H'$ . When  $\delta > 0$  and  $(a + \delta) > 0$ , the transition line shifts to lower temperature.

#### IV. Discussion

Table 1 summarizes the effect of the inclusion of gauche conformations of the amphiphile molecules on the various transition lines in the phase diagram of a Langmuir monolayer.

For transitions that are induced by a change in the surface pressure, the tilting transitions, the transition lines shift toward lower surface pressure. This is the direction expected given the results of simulations that predict a smaller tilt angle for a more flexible amphiphile molecule.<sup>51</sup> The monolayer can respond to a reduction of the surface pressure either by adopting a nonzero collective tilt or by the formation of gauche defects. If the amphiphile molecules support the occurrence of gauche conformations, then it occurs at the expense of the tilting transition. The corollary of this statement is that, for given amphiphile chain length, the tilting transition can be induced by reduction of the surface pressure below the value required to induce that transition in rigid molecules. In addition, the *L*<sub>2d</sub>  $\leftrightarrow$  *O*<sub>v</sub> transition, which involves a change from NN to NNN tilting and is induced by increasing the temperature, has a transition line that shifts to higher temperature when gauche conformations are present. Following the same argument as above, the monolayer can respond to an increase of temperature either by changing the azimuthal angle from NN to NNN or by the acceptance of gauche conformations. The appearance of the later is at the expense of the transition from NN to NNN tilting, so that a higher temperature is required to trigger the transition than in the absence of gauche conformations. For transitions that are induced by lowering the temperature, namely, the crystallization transitions, the choice of sign of the coupling coefficient between the gauche conformation order parameter and the herringbone order parameter is not obvious. It is likely that the gauche defects will disturb the ability of the molecule to arrange in an ordered structure, i.e.,  $\delta > 0$ . Then the transition lines shift to lower temperature, given some restrictions on the magnitude of  $\delta$ . However, we cannot exclude the possibility that the higher lateral cross section that the molecules

**Table 1. The Effect of Gauche Conformations of an Amphiphile Molecule on the Transition Lines in the Phase Diagram of a Langmuir Monolayer**

transition	order of transition	coupled order parameter	coupling coefficient	shift of transition line toward
LS $\leftrightarrow$ O <sub>v</sub>	2	$\eta$	$\delta > 0$	lower surface pressure
LS $\leftrightarrow$ L <sub>2d</sub>	2	$\eta$	$\delta > 0$	lower surface pressure
O <sub>v</sub> $\leftrightarrow$ L <sub>2d</sub>	1	$\eta, \beta$	$\delta < 0$	higher temperature
LS $\leftrightarrow$ S	1	$\varphi$	$\delta < 0$	higher temperature
LS $\leftrightarrow$ S	1	$\varphi$	$\delta > 0$	lower temperature for $-a < \delta G/4H$
S $\leftrightarrow$ CS	1	$\psi$	$\delta < 0$	higher temperature
S $\leftrightarrow$ CS	1	$\psi$	$\delta > 0$	lower temperature for $-a < \delta G/4H$
S $\leftrightarrow$ L <sub>2'</sub>	2	$\eta$	$\delta > 0$	lower surface pressure
CS $\leftrightarrow$ L <sub>2''</sub>	2	$\eta$	$\delta > 0$	lower surface pressure
L <sub>2d</sub> $\leftrightarrow$ L <sub>2h</sub>	1	$\psi$	$\delta < 0$	higher temperature for $a(a + \delta) > G\delta^2/4H$
L <sub>2d</sub> $\leftrightarrow$ L <sub>2h</sub>	1	$\psi$	$\delta > 0$	lower temperature for $(a + \delta) > 0$

have when gauche conformations are present (even without rotational motion around their long axes) will favor phases with higher packing efficiency (the crystalline phases). In this case  $\delta < 0$  and the transition lines shift to higher temperature. We are unaware of any experimental or computational results that would suggest one or the other of these two possibilities.

The phase diagram deduced by the Landau theory analysis appears to provide a satisfactory explanation of the observed polymorphism of the monolayer. Note, however, that the success of the theory depends crucially on the assumption that it is possible to have one-dimensional ordering of the molecular backbones in the monolayer, since it is the coupling of that one-dimensional order with the collective tilt that generates the great diversity of structures and associated phases. We argue that the success of the analysis suggests that the three-

dimensional character of the system is important. Specifically, the inclusion of the tilt degree of freedom is a surrogate for out-of-plane motion by the amphiphile molecules. There are also characteristic properties of the mesophases of the monolayer that have the unique signature of two-dimensional systems (hexatic structure), so a monolayer is likely an example of a mixed dimensional system.

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