

Ising-like model of tilted phase transitions in Langmuir monolayers

Y. V. Sukhinin*

Kirensky Institute of Physics, 660036, Krasnoyarsk, Russia

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Two Ising models on a rectangular lattice (σ_1 model and σ_2 model) linked to three- and four-spin interactions are used to describe the sequence of tilted phase transitions in monolayers of amphiphilic long-chain molecules on an air-water surface. Starting from Morse atom-atom potentials self-consistent equations for basic thermal averages are derived in terms of a mean-field approximation. We employ the model for $\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$ at two values of the molecule density and obtain all known tilted phases, including an intermediate one.

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I. INTRODUCTION

Insoluble molecular monolayers at an air-water surface (Langmuir monolayers) exhibit very rich thermodynamical behavior.¹⁻⁷ To describe the phase transitions in monolayers of long-chain molecules, various theoretical⁸⁻¹⁵ and computational¹⁶⁻¹⁹ techniques are used. Among condensed states of Langmuir monolayers are phases with collective tilt about the water surface of long-axis amphiphilic molecules in a favorite direction. In the tilted phases the heads of amphiphilic molecules are packed in a centered rectangular lattice, the tilt is along one of a two symmetry directions of the lattice, and a backbone plane of the molecules about their long axis is either twofold orientational disordered or herringbone (pseudoherringbone) ordered. It is seen that we have four possible angular positions. To obtain the tilted phase transitions in the monolayers of long-chain molecules two Ising models are used (σ_1 model and σ_2 model).

Our model consists of a two-dimensional orthorhombic array $\{\mathbf{n}\}$ of amphiphilic molecules. The array of molecules can be represented by a two-dimensional lattice $\mathbf{n} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2$, where n_1 and n_2 are integers and unit-cell vectors are

$$\mathbf{a}_1 = (b/2, a/2), \quad \mathbf{a}_2 = (b/2, -a/2), \quad (1)$$

where a and b are the lattice spacing of a face-centered rectangular lattice (Fig. 1). The molecules are regarded as a rigid body; i.e., bond lengths and angles are fixed. The angular position of the molecules is represented by the Eulerian angles $\Omega_{\mathbf{n}} = (\varphi_{\mathbf{n}}, \theta_{\mathbf{n}}, \chi_{\mathbf{n}})$. The azimuth and the tilt of the long axis of the molecules are described accordingly: $\theta_{\mathbf{n}}$, $\varphi_{\mathbf{n}}$, and $\chi_{\mathbf{n}}$ describe the rotation of the molecule about the long axis (Fig. 1). The coordinates of the i th atom of the molecule at the \mathbf{n} site,

$$\mathbf{r}_{\mathbf{n}i} = \mathbf{n} + T(\Omega_{\mathbf{n}})\mathbf{r}_{0i}, \quad (2)$$

where $T(\Omega_{\mathbf{n}})$ is the Euler rotational matrix and \mathbf{r}_{0i} the coordinates of the atom for the case $\theta = \varphi = \chi = 0$. Atoms of nearest-neighbor (NN) molecules at sites \mathbf{n} and \mathbf{m} interact through a pair potential of the form

$$V_{\mathbf{n}i, \mathbf{m}j} = V_0 \{ \exp[-2\kappa(R - r_{\mathbf{n}i, \mathbf{m}j})] - 2 \exp[-\kappa(R - r_{\mathbf{n}i, \mathbf{m}j})] \}, \quad (3)$$

where $r_{\mathbf{n}i, \mathbf{m}j} = |\mathbf{r}_{\mathbf{n}i} - \mathbf{r}_{\mathbf{m}j}|$ is the distance between atoms i and j , the molecules, and V_0 , R , and κ are interaction parameters which depend on the type of atoms. The parameters for hy-

drogen, carbon, and oxygen atoms are given in Table I.

II. THE MODEL

Taking into account the symmetry of the lattice we assume that in the high-temperature phase a molecule may occupy one of four equilibrium angular positions

$$\varphi_{\mathbf{n}} = \pi(\sigma_{1\mathbf{n}} + 1)/2 + \varphi_0\sigma_{2\mathbf{n}}, \quad \theta_{\mathbf{n}} = \theta_0, \quad \chi_{\mathbf{n}} = \chi_0\sigma_{2\mathbf{n}}, \quad (4)$$

where $\sigma_{1\mathbf{n}}, \sigma_{2\mathbf{n}} = \pm 1$, $\varphi_0, \theta_0, \chi_0$ are angles which minimize the system energy in the phase. Summing Eq. (3) over all atoms, we obtain the potential as a function $\sigma_{1\mathbf{n}}$ and $\sigma_{2\mathbf{n}}$ only:

$$V(\sigma_{1\mathbf{n}}, \sigma_{2\mathbf{n}}; \sigma_{1\mathbf{m}}, \sigma_{2\mathbf{m}}) = \sum_{i,j} V_{\mathbf{n}i, \mathbf{m}j}. \quad (5)$$

Then for any configuration $\{\sigma_{1\mathbf{n}}\}, \{\sigma_{2\mathbf{n}}\}$ the system energy is

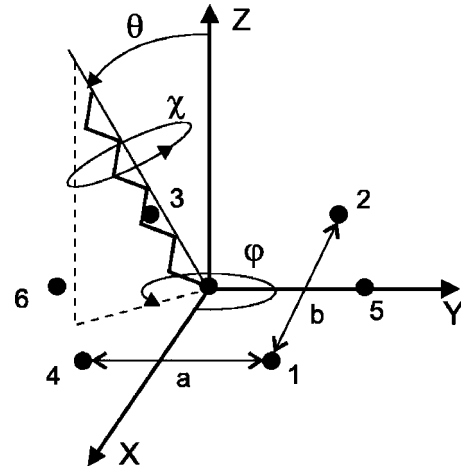


FIG. 1. Schematic diagram showing the rotational position of long-chain zigzag molecules. Angles θ and φ are the tilt angle and tilt direction of the chain, respectively, and χ characterizes the rotation angle about the long axes of the molecule. The black circles indicate the positions of a head of the chain molecules. Lattice spacings a and b are parameters of a face-centered rectangular lattice; integers 1, ..., 6 are the numbers of neighbors of a central molecule.

TABLE I. Interaction parameters.

	H-H ^a	C-C ^a	O-O ^a	H-C ^b	H-O ^b	C-O ^b
V_0 (K)	6.01	33.72	61.52	14.22	19.21	45.55
R (Å)	2.91	3.70	3.25	3.34	3.06	3.52
k (Å ⁻¹)	1.6	1.9	1.3	1.75	1.45	1.46

^aThe potential parameters for the H-H and C-C interactions and the potential parameters for the O-O interactions were taken from Refs. 20 and 21, respectively. We fitted these potentials to the potential (3) by requiring the two potentials to have the same well depth, equilibrium separation, and second derivative with respect to a distance at the equilibrium separation.

^bAll mixed parameters were obtained through combining rules $V_0^{ij} = \sqrt{V_0^{ii}V_0^{jj}}$, $\kappa_{ij} = \frac{1}{2}(\kappa_{ii} + \kappa_{jj})$, $R_{ij} = \frac{\kappa_{ii}R_{ii} + \kappa_{jj}R_{jj}}{\kappa_{ii} + \kappa_{jj}}$.

$$E = \frac{1}{2} \sum_{\mathbf{nm}} V(\sigma_{1\mathbf{n}}, \sigma_{2\mathbf{n}}; \sigma_{1\mathbf{m}}, \sigma_{2\mathbf{m}}). \quad (6)$$

In order to simplify expression (6), we introduce the projection operators $\sigma_{1\mathbf{n}}^\pm = (1 \pm \sigma_{1\mathbf{n}})/2$ and $\sigma_{2\mathbf{n}}^\pm = (1 \pm \sigma_{2\mathbf{n}})/2$. Then using the identity²²

$$V(\sigma_{1\mathbf{n}}, \sigma_{2\mathbf{n}}; \sigma_{1\mathbf{m}}, \sigma_{2\mathbf{m}}) = V(\sigma_{1\mathbf{n}}, \sigma_{2\mathbf{n}}; \sigma_{1\mathbf{m}}, \sigma_{2\mathbf{m}})(\sigma_{1\mathbf{n}}^+ + \sigma_{1\mathbf{n}}^-)$$

$$(\sigma_{2\mathbf{n}}^+ + \sigma_{2\mathbf{n}}^-)(\sigma_{1\mathbf{m}}^+ + \sigma_{1\mathbf{m}}^-)(\sigma_{2\mathbf{m}}^+ + \sigma_{2\mathbf{m}}^-) = \sigma_{1\mathbf{n}}^+ \sigma_{2\mathbf{n}}^+ \sigma_{1\mathbf{m}}^+ \sigma_{2\mathbf{m}}^+$$

$$V_{\mathbf{nm}}(+, +; +, +) + \sigma_{1\mathbf{n}}^+ \sigma_{2\mathbf{n}}^+ \sigma_{1\mathbf{m}}^+ \sigma_{2\mathbf{m}}^- V_{\mathbf{nm}}(+, +; +, -) + \dots + \sigma_{1\mathbf{n}}^- \sigma_{2\mathbf{n}}^- \sigma_{1\mathbf{m}}^- \sigma_{2\mathbf{m}}^- V_{\mathbf{nm}}(-, -; -, -), \quad (7)$$

where $V_{\mathbf{nm}}(+, +; +, +) = V(\sigma_{1\mathbf{n}}=1, \sigma_{2\mathbf{n}}=1; \sigma_{1\mathbf{m}}=1, \sigma_{2\mathbf{m}}=1)$, $V_{\mathbf{nm}}(+, +; +, -) = V(\sigma_{1\mathbf{n}}=1, \sigma_{2\mathbf{n}}=1; \sigma_{1\mathbf{m}}=1, \sigma_{2\mathbf{m}}=-1), \dots$, $V_{\mathbf{nm}}(-, -; -, -) = V(\sigma_{1\mathbf{n}}=-1, \sigma_{2\mathbf{n}}=-1; \sigma_{1\mathbf{m}}=-1, \sigma_{2\mathbf{m}}=-1)$, we can write Eq. (5) in terms of $\sigma_{1\mathbf{n}}$ and $\sigma_{2\mathbf{n}}$:

$$E = E_0 + \sum_{\mathbf{n}} \{B_1(\mathbf{n})\sigma_{1\mathbf{n}} + B_2(\mathbf{n})\sigma_{2\mathbf{n}} + B_3(\mathbf{n})\sigma_{1\mathbf{n}}\sigma_{2\mathbf{n}}\} - \frac{1}{2} \sum_{\mathbf{nm}} \{J_1(\mathbf{n}, \mathbf{m})\sigma_{1\mathbf{n}}\sigma_{1\mathbf{m}} + J_2(\mathbf{n}, \mathbf{m})\sigma_{2\mathbf{n}}\sigma_{2\mathbf{m}} + D_1(\mathbf{n}, \mathbf{m})\sigma_{1\mathbf{n}}\sigma_{2\mathbf{n}}\sigma_{1\mathbf{m}}\sigma_{2\mathbf{m}}\} + \sum_{\mathbf{nm}} \{J_3(\mathbf{n}, \mathbf{m})\sigma_{1\mathbf{n}}\sigma_{2\mathbf{m}} + C_1(\mathbf{n}, \mathbf{m})\sigma_{1\mathbf{n}}\sigma_{2\mathbf{n}}\sigma_{1\mathbf{m}} + C_2(\mathbf{n}, \mathbf{m})\sigma_{1\mathbf{n}}\sigma_{2\mathbf{n}}\sigma_{2\mathbf{m}}\}, \quad (8)$$

where sums run over NN molecules and coefficients $E_0, B_1, \dots, B_3, J_1, \dots, J_3, C_1, C_2,$ and D_1 consist of linear combinations of products ± 1 and the potentials (5). The coefficients $B_1, B_2,$ and B_3 are equal to zero due to the symmetry of the system (see the Appendix). To paraphrase, the minimum $E_0 = E_0(\varphi, \theta, \chi)$ with respect to the angles gives equilibrium $\varphi_0, \theta_0, \chi_0$ for Eq. (4). We have obtained Hamiltonian of two superposed Ising models (σ_1 and σ_2) coupled by two-, three-, and four-spin interactions.

III. MEAN-FIELD THEORY

The simplest way of getting an approximate analytic expression for the thermodynamic properties of the model is

usually by means of the mean-field (MF) approximation. In the MF approximation the Hamiltonian (8) can be written as

$$E_{MF} = H_{MF} + \Delta. \quad (9)$$

The term H_{MF} is a function of the variables $\sigma_{1\mathbf{n}}$ and $\sigma_{2\mathbf{n}}$,

$$H_{MF} = - \sum_{\mathbf{n}} \{H_1(\mathbf{n})\sigma_{1\mathbf{n}} + H_2(\mathbf{n})\sigma_{2\mathbf{n}} + H_3(\mathbf{n})\sigma_{1\mathbf{n}}\sigma_{2\mathbf{n}}\}, \quad (10)$$

where

$$H_1(\mathbf{n}) = \sum_{\mathbf{m}} \{J_1(\mathbf{n}, \mathbf{m})\bar{\sigma}_{1\mathbf{m}} - J_3(\mathbf{n}, \mathbf{m})\bar{\sigma}_{2\mathbf{m}} - C_1(\mathbf{n}, \mathbf{m})\overline{\sigma_{1\mathbf{m}}\sigma_{2\mathbf{m}}}\},$$

$$H_2(\mathbf{n}) = \sum_{\mathbf{m}} \{J_2(\mathbf{n}, \mathbf{m})\bar{\sigma}_{2\mathbf{m}} - J_3(\mathbf{n}, \mathbf{m})\bar{\sigma}_{1\mathbf{m}} - C_2(\mathbf{n}, \mathbf{m})\overline{\sigma_{1\mathbf{m}}\sigma_{2\mathbf{m}}}\},$$

$$H_3(\mathbf{n}) = \sum_{\mathbf{m}} \{D_1(\mathbf{n}, \mathbf{m})\overline{\sigma_{1\mathbf{m}}\sigma_{2\mathbf{m}}} - C_1(\mathbf{n}, \mathbf{m})\bar{\sigma}_{1\mathbf{m}} - C_2(\mathbf{n}, \mathbf{m})\bar{\sigma}_{2\mathbf{m}}\},$$

and $\bar{\sigma}_{1\mathbf{n}}$, and $\bar{\sigma}_{2\mathbf{n}}$, and $\overline{\sigma_{1\mathbf{n}}\sigma_{2\mathbf{n}}}$ are the thermal averages at site \mathbf{n} .

The second term from Eq. (9),

$$\Delta = E_0 + \frac{1}{2} \sum_{\mathbf{n}, \mathbf{m}} \{J_1(\mathbf{n}, \mathbf{m})\bar{\sigma}_{1\mathbf{n}}\bar{\sigma}_{1\mathbf{m}} + J_2(\mathbf{n}, \mathbf{m})\bar{\sigma}_{2\mathbf{n}}\bar{\sigma}_{2\mathbf{m}} + D_1(\mathbf{n}, \mathbf{m})\overline{\sigma_{1\mathbf{n}}\sigma_{2\mathbf{n}}\sigma_{1\mathbf{m}}\sigma_{2\mathbf{m}}}\} - \sum_{\mathbf{n}, \mathbf{m}} \{C_1(\mathbf{n}, \mathbf{m})\bar{\sigma}_{1\mathbf{n}}\overline{\sigma_{1\mathbf{m}}\sigma_{2\mathbf{m}}} + C_2(\mathbf{n}, \mathbf{m})\bar{\sigma}_{2\mathbf{n}}\overline{\sigma_{1\mathbf{m}}\sigma_{2\mathbf{m}}} + J_3(\mathbf{n}, \mathbf{m})\bar{\sigma}_{1\mathbf{n}}\bar{\sigma}_{2\mathbf{m}}\}, \quad (11)$$

is a constant with regard to the variables $\sigma_{1\mathbf{n}}, \sigma_{2\mathbf{n}}$.

The single-site partition function produced by Hamiltonian (10) is

$$Z_{\mathbf{n}} = 4\{\cosh(h_{1\mathbf{n}})\cosh(h_{2\mathbf{n}})\cosh(h_{3\mathbf{n}}) + \sinh(h_{1\mathbf{n}})\sinh(h_{2\mathbf{n}})\sinh(h_{3\mathbf{n}})\}, \quad (12)$$

where $h_{\alpha\mathbf{n}} = H_{\alpha}(\mathbf{n})/T$. We have chosen a unit system with the Boltzmann constant equal to unity.

The basic averages are obtained by a self-consistent method from a request that an approximate free-energy function

TABLE II. Coupling coefficients (8), measured in units of K. Numbers of columns correspond to numbers of the nearest neighbors according to Fig. 1.

	1	2	3	4	5	6
J_1	121.3	121.3	121.3	121.3	-52.5	-52.5
J_2	-60.3	-60.3	-60.3	-60.3	71.8	71.8
J_3	-14.9	-14.9	14.9	14.9	30.5	-30.5
J_4	14.9	14.9	-14.9	-14.9	-30.5	30.5
C_1	79.4	-79.4	79.4	-79.4	0.0	0.0
C_2	79.4	-79.4	79.4	-79.4	0.0	0.0
C_3	-2.7	2.7	2.7	-2.7	0.0	0.0
C_4	2.7	-2.7	-2.7	2.7	0.0	0.0
D_1	52.2	52.2	52.2	52.2	85.6	85.6

$$F = -T \ln Sp \exp[-E_{MF}/T] = -T \sum_{\mathbf{n}} \ln Z_{\mathbf{n}} + \Delta \quad (13)$$

be minimized by the correct choice of the averages²³

$$\bar{\sigma}_{1\mathbf{n}} = (\tanh h_{1\mathbf{n}} + \tanh h_{2\mathbf{n}} \tanh h_{3\mathbf{n}})/D,$$

$$\bar{\sigma}_{2\mathbf{n}} = (\tanh h_{2\mathbf{n}} + \tanh h_{1\mathbf{n}} \tanh h_{3\mathbf{n}})/D,$$

$$\overline{\sigma_{1\mathbf{n}}\sigma_{2\mathbf{n}}} = (\tanh h_{3\mathbf{n}} + \tanh h_{1\mathbf{n}} \tanh h_{2\mathbf{n}})/D,$$

$$D = 1 + \tanh h_{1\mathbf{n}} \tanh h_{2\mathbf{n}} \tanh h_{3\mathbf{n}}. \quad (14)$$

Whenever we obtain several solutions of the system (14), we select the solution which minimizes the free energy given by Eq. (13). Note that in writing the free energy (13) as we have, we have missed terms which are uncoupled with variables $\sigma_{1\mathbf{n}}$ and $\sigma_{2\mathbf{n}}$ because one cannot change the minimization conditions (14).

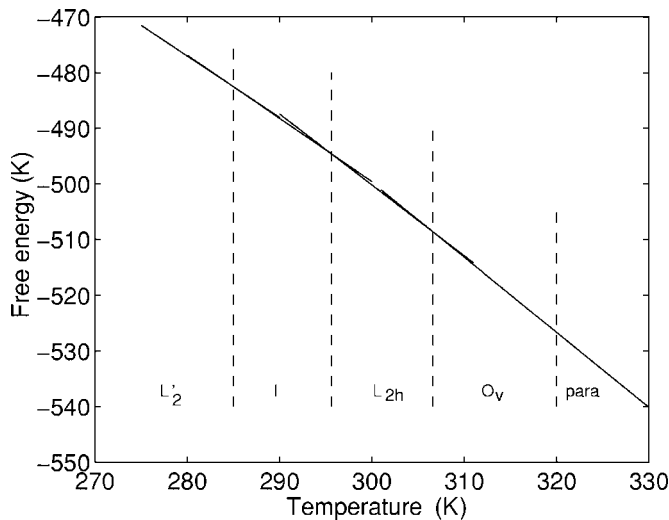


FIG. 2. C_{20} phase diagram versus temperature at area per molecule, $S_0=20.01 \text{ \AA}^2$. Dashed lines separate phases from each other. The phases presented are disordered untilted paraphase “para,” tilted hexatic phase O_v , one-dimensional crystal phases L_{2h} , L'_2 , and I the intermediate phase.

IV. PHASE DIAGRAM

Let us use the model in order to consider successive phase transitions in Langmuir monolayers of eicosanoic acid [$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$ or C_{20}]. First, fatty acid molecules have simple structure. Second, C_{20} monolayers are known to exhibit a variety of positionally ordered tilted phases. Third, in a first approximation for a given length of the molecules we can neglect the effect of the molecule-liquid interface. The parameters of atom-atom interactions between different chains are listed in Table I. Bond angles are constrained ideal valence angles. Bond lengths are set equal to the following values: $l_{\text{CC}}=1.53 \text{ \AA}$, $l_{\text{CH}}=1.04 \text{ \AA}$, $l_{\text{CO}}=1.25 \text{ \AA}$, and $l_{\text{OH}}=1.04 \text{ \AA}$. At first, we calculate equilibrium angles φ_0 , θ_0 , and ψ_0 and equilibrium parameters a and b of the lattice. For the surface area per molecule, $S_0=20.01 \text{ \AA}^2$, the minimum E_0 of Eq. (8) yields the following equilibrium angles: $\varphi_0=32^\circ$, $\theta_0=1.7^\circ$, and $\psi_0=180^\circ$ and $a=4.81 \text{ \AA}$ and $b=8.33 \text{ \AA}$ lattice constants. This lattice is the hexagonal lattice slightly stretched in the next-nearest-neighbor (NNN) direction.

Next, using the equilibrium values we obtain the coupling constants J_1 , J_2 , J_3 , C_1 , C_2 , and D_1 . They are shown in Table II for the nearest neighbors enumerated according to Fig. 1.

Third, we calculate solutions of Eqs. (14) as a function of temperature. Finally, we choose the solutions that give the minimum to the free energy (13). Figure 2 shows the calculated phase diagram plotted as a function of temperature. Before describing the solutions of Eqs. (14), it is useful to find a thermal average of atom coordinates. Using Eq. (4) in Euler’s matrix $T(\Omega_{\mathbf{n}})$, we can write

$$\begin{aligned} \bar{X}_{\mathbf{n}i} = & \bar{\sigma}_{1\mathbf{n}}(\cos \varphi_0 \cos \theta_0 \cos \chi_0 - \sin \varphi_0 \sin \chi_0)(\mathbf{r}_{0i})_x \\ & + \overline{\sigma_{1\mathbf{n}}\sigma_{2\mathbf{n}}}(\cos \varphi_0 \cos \theta_0 \sin \chi_0 + \sin \varphi_0 \cos \chi_0)(\mathbf{r}_{0i})_y \\ & - \bar{\sigma}_{1\mathbf{n}} \cos \varphi_0 \sin \theta_0(\mathbf{r}_{0i})_z, \end{aligned}$$

$$\begin{aligned} \bar{Y}_{\mathbf{n}i} = & -\overline{\sigma_{1\mathbf{n}}\sigma_{2\mathbf{n}}}(\sin \varphi_0 \cos \theta_0 \cos \chi_0 + \cos \varphi_0 \sin \chi_0)(\mathbf{r}_{0i})_x \\ & + \bar{\sigma}_{1\mathbf{n}}(\sin \varphi_0 \cos \theta_0 \sin \chi_0 - \cos \varphi_0 \cos \chi_0)(\mathbf{r}_{0i})_y \\ & - \overline{\sigma_{1\mathbf{n}}\sigma_{2\mathbf{n}}} \sin \varphi_0 \sin \theta_0(\mathbf{r}_{0i})_z, \end{aligned}$$

$$\begin{aligned} \bar{Z}_{ni} = & -\sin \theta_0 \cos \chi_0(\mathbf{r}_{0i})_x + \bar{\sigma}_{2n} \sin \theta_0 \sin \chi_0(\mathbf{r}_{0i})_y \\ & + \cos \theta_0(\mathbf{r}_{0i})_z, \end{aligned} \quad (15)$$

where \bar{X}_{ni} , \bar{Y}_{ni} , and \bar{Z}_{ni} are the average coordinates of the i th atom of the molecule at the \mathbf{n} site.

Let us list the phases given.

(i) The simplest solution of Eqs. (14) describes a paraphase. In this phase neither $\bar{\sigma}_{1n}$ nor $\bar{\sigma}_{2n}$ (nor anything else) is ordered. The average tilt of the molecules equal zero, which is easy to see from Eq. (15), and in this sense, paraphase is untilt phase.

(ii) O_v phase (tilt direct NNN) in which σ_1 is ordered ferromagnetically $\bar{\sigma}_{1n} = \sigma_1 \neq 0$ but $\bar{\sigma}_{2n} = \sigma_{1n}\sigma_{2n} = 0$. The transition temperature T_c and the corresponding structure of ordered phase is determined by the wave vector \mathbf{k}_0 for which the Fourier transform of the interactions $J_1(\mathbf{n}, \mathbf{m})$,

$$J_{1\mathbf{k}} = \sum_{\mathbf{m}} J_1(\mathbf{n}, \mathbf{m}) \exp[i\mathbf{k}(\mathbf{n} - \mathbf{m})], \quad (16)$$

takes on the maximum value and $T_c = J_{1\mathbf{k}_0}$. The transform (11) under nearest-neighboring chain-chain coupling is given by the following expression:

$$\begin{aligned} T_c = & 2J_1(\mathbf{a}_1) \cos 2\pi\xi_1 + 2J_1(\mathbf{a}_2) \cos 2\pi\xi_2 \\ & + 2J_1(\mathbf{a}_1 - \mathbf{a}_2) \cos 2\pi(\xi_1 - \xi_2), \end{aligned}$$

where the wave vector $\mathbf{k} = \xi_1 \mathbf{b}_1 + \xi_2 \mathbf{b}_2$ is written about the reciprocal lattice vectors

$$\mathbf{b}_1 = 2\pi(1/b, 1/a), \quad \mathbf{b}_2 = 2\pi(1/b, -1/a), \quad (17)$$

and $J_1(\mathbf{a}_1)$, $J_1(\mathbf{a}_2)$, and $J_1(\mathbf{a}_1 - \mathbf{a}_2)$ are the coupling constants along the vectors $\pm \mathbf{a}_1$, $\pm \mathbf{a}_2$, and $\pm(\mathbf{a}_2 - \mathbf{a}_1)$ accordingly. The O_v phase structure is described by the wave vector $\mathbf{k}_1 = (0, 0)$.

(iii) L_{2h} phase (tilt direct NN) in which σ_1 is ordered ferromagnetically $\bar{\sigma}_{1n} = \sigma_1$, but σ_{2n} and product $\sigma_{1n}\sigma_{2n}$ are ordered antiferromagnetically $\bar{\sigma}_{2n} = \pm \sigma_2$, $\sigma_{1n}\sigma_{2n} = \pm \sigma_3$. The L_{2h} phase structure is described by the wave vectors $\mathbf{k}_1 = (0, 0)$ and $\mathbf{k}_2 = \mathbf{k}_3 = (0.5, 0.5)$. It should be noted that the parameters of H-H and C-C interactions from Table I were obtained by requiring the temperature of the phase transition $O_v \rightarrow L_{2h}$ to be 310 K approximately.^{24,25} Initial data for the fit used the atom-atom parameters from Ref. 20.

(iv) The direction of the tilt in chiral phase I is intermediate between NN and NNN ones. In Table III the order parameters and corresponding wave vectors at the beginning and at the ending of the phase are shown. Note that in this phase an ordering of molecules is sinusoidally modulated according to the wave vectors of Table III.

(v) The phase L'_2 (tilt direct NNN) in which $\sigma_{1n}\sigma_{2n}$ is ordered ferromagnetically $\sigma_{1n}\sigma_{2n} = \sigma_3$ but σ_{1n} and σ_{2n} are ordered antiferromagnetically $\bar{\sigma}_{1n} = \pm \sigma_1$, $\bar{\sigma}_{2n} = \pm \sigma_2$. The L'_2 phase structure is described by the wave vectors $\mathbf{k}_3 = (0, 0)$ and $\mathbf{k}_1 = \mathbf{k}_2 = (0.5, 0.5)$.

TABLE III. The order parameters and wave vectors in the intermediate phase.

T (K)	354	346
$\bar{\sigma}_{1n}$	0.61	0.21
$\bar{\sigma}_{2n}$	0.24	0.03
$\sigma_{1n}\sigma_{2n}$	0.76	0.71
\mathbf{k}_1	(0.02, 0.47)	(0.43, 0.45)
\mathbf{k}_2	(0.49, 0.48)	(0.48, 0.48)
\mathbf{k}_3	(0.3, 0.41)	(0.03, 0.34)

In addition to the phases shown in Fig. 2 we also take into consideration the L_{2d} phase (tilt direct NN) in which $\sigma_{1n}\sigma_{2n}$ is ordered ferromagnetically $\sigma_{1n}\sigma_{2n} = \sigma_3 \neq 0$ but $\bar{\sigma}_{1n} = 0$ and $\bar{\sigma}_{2n} = 0$. As the surface area per molecule, S_0 , increasing to 20.92 Å² and above, the O_v phase free-energy minimum about the angles φ_0 , θ_0 , and ψ_0 and lattice parameters a and b exceeds 1 for L_{2d} phase and therefore the paraphase $\rightarrow L_{2d}$ phase transition occurs. For the density, equilibrium angles are equal to $\varphi_0 = 43^\circ$, $\theta_0 = 5.6^\circ$, and $\psi_0 = 180^\circ$ and equilibrium lattice parameters are equal to $a = 4.95$ Å and $b = 8.53$ Å. For these values phase transition paraphases $\rightarrow L_{2d} \rightarrow L_{2h} \rightarrow L''$ take place at 351 K, 302 K, and 295 K, respectively. Note that the lattice is obtained by a stretching hexagonal lattice in the NN direction.

V. SUMMARY

In conclusion, we have developed an Ising-like model for a two-dimensional rectangular lattice of long-chain molecules. Two coupling Ising models allow us to describe the sequence of tilted phase transitions in the monolayers. Tilted phase transitions of Langmuir monolayers are due to a freezing of the jumps of the long chains between fourfold-degenerated angular positions. Both the succession of ordering and its structure depend on the density of long chains by means of coupling constants. The lattice distortion plays a crucial role in determining the phase transition sequence. The distortion of the lattice has been indirectly taken into consideration by minimization of free energy with respect to lattice constants. The model has been used to describe successive tilted phase transitions of eicosanoic acid monolayers. We have just chosen such densities of chains for which all known phase transitions for these monolayers can be obtained. The temperatures of phase transitions calculated in the MF approximation can be regarded as acceptable for the approximation.

APPENDIX

The coefficient E_0 from Eq. (8) is

$$E_0 = \frac{1}{16} \sum_{\mathbf{n}, \mathbf{m}} \{V_{\mathbf{nm}}(+, +; +, +) + V_{\mathbf{nm}}(+, +; +, -) + V_{\mathbf{nm}}(+, +; -, +) + V_{\mathbf{nm}}(+, -; +, +) + V_{\mathbf{nm}}(+, +; -, -) + V_{\mathbf{nm}}(+, -; +, -) + V_{\mathbf{nm}}(+, -; -, +) + V_{\mathbf{nm}}(+, -; -, -) + V_{\mathbf{nm}}(-, +; +, +) + V_{\mathbf{nm}}(-, +; +, -) + V_{\mathbf{nm}}(-, +; -, +) + V_{\mathbf{nm}}(-, -; +, +) + V_{\mathbf{nm}}(-, +; -, -) + V_{\mathbf{nm}}(-, -; +, -) + V_{\mathbf{nm}}(-, -; -, +) + V_{\mathbf{nm}}(-, -; -, -)\}.$$

The coefficients $B_1(\mathbf{n})$, $B_2(\mathbf{n})$, and $B_3(\mathbf{n})$ from Eq. (8) are

$$B_1(\mathbf{n}) = \frac{1}{16} \sum_{\mathbf{m}} \{V_{\mathbf{nm}}(+, +; +, +) + V_{\mathbf{nm}}(+, +; +, -) + V_{\mathbf{nm}}(+, +; -, +) + V_{\mathbf{nm}}(+, -; +, +) + V_{\mathbf{nm}}(+, +; -, -) + V_{\mathbf{nm}}(+, -; +, -) + V_{\mathbf{nm}}(+, -; -, +) + V_{\mathbf{nm}}(+, -; -, -) - V_{\mathbf{nm}}(-, +; +, +) - V_{\mathbf{nm}}(-, +; +, -) - V_{\mathbf{nm}}(-, +; -, +) - V_{\mathbf{nm}}(-, -; +, +) - V_{\mathbf{nm}}(-, +; -, -) - V_{\mathbf{nm}}(-, -; +, -) - V_{\mathbf{nm}}(-, -; -, +) - V_{\mathbf{nm}}(-, -; -, -)\},$$

$$B_2(\mathbf{n}) = \frac{1}{16} \sum_{\mathbf{m}} \{V_{\mathbf{nm}}(+, +; +, +) + V_{\mathbf{nm}}(+, +; +, -) + V_{\mathbf{nm}}(+, +; -, +) - V_{\mathbf{nm}}(+, -; +, +) + V_{\mathbf{nm}}(+, +; -, -) - V_{\mathbf{nm}}(+, -; +, -) + V_{\mathbf{nm}}(+, -; -, +) - V_{\mathbf{nm}}(+, -; -, -) + V_{\mathbf{nm}}(-, +; +, +) + V_{\mathbf{nm}}(-, +; +, -) + V_{\mathbf{nm}}(-, +; -, +) - V_{\mathbf{nm}}(-, -; +, +) + V_{\mathbf{nm}}(-, +; -, -) - V_{\mathbf{nm}}(-, -; +, -) - V_{\mathbf{nm}}(-, -; -, +) - V_{\mathbf{nm}}(-, -; -, -)\},$$

$$B_3(\mathbf{n}) = \frac{1}{16} \sum_{\mathbf{m}} \{V_{\mathbf{nm}}(+, +; +, +) + V_{\mathbf{nm}}(+, +; +, -) + V_{\mathbf{nm}}(+, +; -, +) - V_{\mathbf{nm}}(+, -; +, +) + V_{\mathbf{nm}}(+, +; -, -) - V_{\mathbf{nm}}(+, -; +, -) + V_{\mathbf{nm}}(+, -; -, +) - V_{\mathbf{nm}}(+, -; -, -) - V_{\mathbf{nm}}(-, +; +, +) - V_{\mathbf{nm}}(-, +; +, -) - V_{\mathbf{nm}}(-, +; -, +) + V_{\mathbf{nm}}(-, -; +, +) - V_{\mathbf{nm}}(-, +; -, -) + V_{\mathbf{nm}}(-, -; +, -) + V_{\mathbf{nm}}(-, -; -, +) + V_{\mathbf{nm}}(-, -; -, -)\}.$$

These coefficients are equal to zero because in the sums for any term we have an opposite one. For example, for $B_1(\mathbf{n})$ we have $V_{\mathbf{nm}+\mathbf{a}_1}(+, +; +, +) - V_{\mathbf{nm}-\mathbf{a}_1}(-, +; -, +) = 0$, $V_{\mathbf{nm}-\mathbf{a}_2}(+, +; +, +) - V_{\mathbf{nm}+\mathbf{a}_2}(-, +; -, +) = 0, \dots$, $V_{\mathbf{nm}+\mathbf{a}_1}(+, +; +, -) - V_{\mathbf{nm}-\mathbf{a}_1}(-, +; -, -) = 0$, and so on.

*Electronic address: sukhinin@ktk.ru

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