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Modeling of the behavior and statistical analysis of compressibility in the process of Langmuir monolayer structurization

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Abstract. An approach has been developed to perform data processing for experiments on two-dimensional phase transition of first order. The approach represents itself the two stage filtration with subsequent merging of processed data and comparison with simulation results based on geometro-thermodynamical methods. The approach has been successfully applied to description of the phase transition in compressed monolayers of steric acid.

1. Introduction

Development of formation methods for two-dimensional (2D) solid-state perfect structures, which can operate at room temperature, is an important problem of flexible electronics. Langmuir-Blodgett (LB) technique can be used to produce almost perfect two-dimensional structures, provided that the conditions on a phase boundary are under the control [1].

To utilize LB monolayers as a material for nanoelectronics it is necessary to correlate structural changes in a metastable compressed monolayer with changes of phenomenological parameters of the monolayer (e.g., compressibility coefficient). This requires a statistical analysis of experimental dependences of the surface tension $\tilde{\pi}$ upon the area A per molecule, followed by compressibility calculation.

When modeling the Langmuir monolayer compression by Monte Carlo methods, a metastable state is excluded from consideration that does not allow for such a control [2]. A compressibility κ , for $\tilde{\pi}-A$ isotherms being dependencies of surface tension $\tilde{\pi}$ on an area A per one molecule, presents itself a derivative from the dependence $\ln A(\tilde{\pi})$ over $\tilde{\pi}$. But, instead of it, the "apparent" compressibility $\kappa_{\text{app}} = 1/K'$ being an inverse elasticity of a Langmuir monolayer is calculated [3–5].

To construct the dependence of compressibility coefficient in the whole range of the surface pressure $\tilde{\pi}$, it is necessary to use the procedure of the statistical data processing on a huge experimental data set due to large fluctuations in critical regions for 2D phase transitions. Nowadays such data processing of $\tilde{\pi}-A$ compression isotherms have not been proposed.

In [6–8], a geometric approach to the thermodynamics of the first order phase transitions in compressed monolayers on the interphase boundary of air/water subphase has been developed.

The goal of this work is to propose a method of compression isotherms statistical analysis for metastable Langmuir monolayers. It allows to evaluate the compressibility coefficient based on experimental data. We model the 2D phase transitions of first order using geometrodynamical methods and demonstrate that theoretical predictions and experimentally obtained compressibility of monolayers of stearic acid are close to each other.



2. Materials and methods

Langmuir monolayers are fabricated on an automated home-built Langmuir trough with controlled deposition on a substrate [9]. Hexan solution of stearic acid was dripped with the help of a micropipette on a liquid subphase surface. Langmuir monolayers were obtained by compressing of stearic acid molecules on air / aqueous subphase interface. Deionized water was used as a subphase for stearic acid monolayer formation.

3. Data processing

In this paper, we propose a method of statistical analysis when at first stage we smoothen 2D fluctuations of the vector $\vec{r}_i \equiv (\tilde{\pi}_i, A_i)$ over an interval of n_1 values of the surface tension $\tilde{\pi}_{i+j}$ and

corresponding to them values of the area A_{i+j} per one molecule: $\vec{r}_i \equiv (\tilde{\pi}_i, A_i) = \frac{1}{n_1} \sum_{j=-n_1/2}^{n_1/2} \vec{r}_{i+j}$. Then, a

filtering procedure based on the sliding mean with given window width m_1 is applied to the smoothed set, when an experimental value is to replace by a mean value obtained from the m_1 nearest points as:

$\tilde{\pi}_i \rightarrow \langle \tilde{\pi}_i \rangle = \frac{1}{m_1} \sum_{j=-m_1/2}^{m_1/2} \tilde{\pi}_{i+j}$. The filtering on the sliding mean was applied only to the readings of the

surface tension sensor, as its noise prevails over the noise of "inertial" position sensor. To find the compressibility $\kappa(\tilde{\pi})$ of monolayer, the logarithmic derivative of the dependence $A(\tilde{\pi})$ obtained after the data processing with filtering parameters $\{n_1, m_1\}$ was calculated numerically. The existence of scale invariance property of phase transitions was accounted by merging several filtrations of original data.

4. Compressibility of amphiphilic two-dimensional membranes with Finsler–Lagrange space structure

The amphiphilic molecules of fat acids form a monolayer on the surface of the water subphase. Let us consider the motion of a particle in the monolayer under the action of electrocapillary forces that take place on the interface and determine the magnitude of the surface tension σ of such a 2D membrane [10]. The first order phase transition occurs for long compression time $\Delta t \gg 1$ (long observation time). The experimentally measured quantity, interpreted as the surface pressure $\tilde{\pi}$ of the monolayer, is defined by the expression:

$$\tilde{\pi} = \sigma_{\text{H}_2\text{O}} - \sigma_{\text{hydrocomp}} \quad (1)$$

where $\sigma_{\text{H}_2\text{O}}$ is the surface tension of the subphase (e.g., water), $\sigma_{\text{hydrocomp}}$ is the surface tension of the subphase with hydrate complexes. According to (1), molecules which leave the hydrate complexes do not contribute to the experimentally measurable value of $\tilde{\pi}$. The surface pressure of the hydrated monolayer changes, but as a consequence of the diminishing of the Langmuir monolayer density ρ due to the complexes decay, the increment of surface pressure $\Delta\tilde{\pi}$, observed during the phase transition of Δt , is equal to zero: $\Delta\tilde{\pi} = 0$. In this sense, at the first order phase transition, the parameters of molecules which leave hydrated complexes are hidden from the observer. This allows us to introduce an evolution parameter τ as a parameter of the current state of the process of the first order phase transition in a hydrated complexes monolayer only. Then, the derivative $\frac{d\Delta\tilde{\pi}}{d\tau}$ is the rate

of surface pressure change for the hydrated complexes monolayer. Since $\frac{\partial(S\tilde{\pi})}{\partial\tau} \propto -\frac{\partial(V\Delta t_{\text{ph}}\tilde{\pi})}{\partial\tau} \propto k_B T \frac{\partial\rho}{\partial\tau} \propto k_B T \tilde{C}$ and $\frac{\partial r}{\partial\tau} \propto C'V$, C' ; \tilde{C} and the temperature $k_B T$ are

constants, and the change of the area S per one molecule is proportional to the square of variation $\delta r(\tau)^2$, then we find a space–time derivative of the compressibility coefficient $\kappa = \frac{1}{S} \frac{\partial S}{\partial \tilde{\pi}}$:

$$\frac{\partial \kappa'_\tau}{\partial r} = -\frac{1}{S \Delta t_{\text{ph}} \partial r \partial \tilde{\pi}} \frac{\partial^2 S}{\partial r \partial \tilde{\pi}} = \frac{2}{k_B T C'' \delta r} \frac{\partial^2 \delta r}{\partial \tau^2} \quad (2)$$

where $\kappa'_\tau = \frac{\partial \kappa}{\partial \tau} \propto \frac{\kappa}{\Delta t_{\text{ph}}}$, $C'' = C' \tilde{C}$, $C', \tilde{C} > 0$; $S \propto \delta r^2$, Δt_{ph} is time of the phase transition, V is a compression rate.

We apply a geometrodynamics of the first order phase transitions in two-dimensional systems to examine metastable compressed monolayers [6–8]. δr is determined by the flag curvature K as $\frac{\partial^2 \delta r(\tau)}{\partial \tau^2} = -K \cdot \delta r$ [11]. We choose the trace B_c of Berwald curvature B_{ikj}^k as K :

$$B_c = g^{ij} B_{ikj}^k = g^{ij} \frac{\partial G^k}{\partial y^i \partial y^k \partial y^j}, \quad \bar{y} = (\xi, \dot{r}, \dot{\varphi}), \quad \xi = \frac{dt}{d\tau}, \dot{r} = \frac{dr}{d\tau}, \dot{\varphi} = \frac{d\varphi}{d\tau}. \quad \text{Here, a vector } G^k \text{ is determined}$$

by equating the variation of action $\int dl_F = \int F(x^j, dx^j)$ to zero. One uses a following metric function $F(x^j, dx^j)$ [6–8]:

$$F^2(x^j, \Delta x^j) = A \frac{\Delta \xi^3}{\Delta r} + B \Delta \xi - C \frac{(\Delta r^2 + r^2 \Delta \varphi^2)}{2c^2} \quad (3)$$

where A , B and C are defined as follows:

$$\begin{aligned} A &= p |V| r^5 e^{\frac{2|V|t}{r}}, \\ B &= mc^2 - p \left(\left(-\frac{4}{3} r^5 + \frac{16}{15} (|V|t) r^4 + \frac{1}{30} (|V|t)^2 r^3 + \frac{1}{45} (|V|t)^3 r^2 + \frac{1}{45} (|V|t)^4 r \right. \right. \\ &\quad \left. \left. + \frac{2}{45} (|V|t)^5 \right) e^{\frac{2|V|t}{r}} - \frac{4}{45} \frac{(|V|t)^6}{r} \text{Ei} \left[\frac{2|V|t}{r} \right] \right), \\ C &= mc^2 \end{aligned}$$

where m is a mass of a particle, $p = \frac{\pi^2 q^2 \rho_0^2}{\varepsilon \varepsilon_0 R_0^2}$ is a parameter dependent on a charge q of monolayer

molecule, density ρ_0 of molecules at initial moment, dielectric constant ε_0 , dielectric permittivity ε of the subphase, and radius R_0 of a radial trough, c is speed of light; r, φ determine a displacement of the particle in the polar coordinate system; a special function Ei is an exponential integral function. The metric tensor is determined through the metric function as follows:

$$g_{ij} = \frac{1}{2} \frac{\partial^2 F^2}{\partial y_i \partial y_j} = \begin{pmatrix} 3A \frac{\dot{\xi}}{\dot{r}} & -\frac{3}{2} A \left(\frac{\dot{\xi}}{\dot{r}} \right)^2 & 0 \\ -\frac{3}{2} A \left(\frac{\dot{\xi}}{\dot{r}} \right)^2 & A \left(\frac{\dot{\xi}}{\dot{r}} \right)^3 - \frac{C}{2c^2} & 0 \\ 0 & 0 & -\frac{C}{2c^2} r^2 \end{pmatrix}. \tag{4}$$

And the components of the vector G^k :

$$G^i(y) = \frac{1}{4} g^{il}(y) \left\{ 2 \frac{\partial g_{jl}}{\partial x^k}(y) - \frac{\partial g_{ik}}{\partial x^l}(y) \right\} y^j y^k \tag{5}$$

are determined as

$$\begin{aligned} G^1 &= \frac{A}{4\Delta} \left[\frac{1}{2} A_t \frac{\dot{\xi}^6}{\dot{r}^4} + B_t \frac{\dot{\xi}^5}{\dot{r}^3} + \frac{1}{2} B_r \frac{\dot{\xi}^4}{\dot{r}^2} + \frac{3}{2} \frac{C}{c^2} r \frac{\dot{\xi}^2 \dot{\varphi}^2}{\dot{r}^2} \right] - \frac{C}{8c^2 \Delta} \left[2A_t \frac{\dot{\xi}^3}{\dot{r}} + B_t \dot{\xi}^2 + 3A_r \dot{\xi}^2 + 3B_r \dot{\xi} \dot{r} \right], \\ G^2 &= \frac{3A}{4\Delta} \left[-\frac{1}{2} A_r \frac{\dot{\xi}^4}{\dot{r}^2} + \frac{1}{2} B_t \frac{\dot{\xi}^4}{\dot{r}^2} + \frac{C}{c^2} r \frac{\dot{\xi} \dot{\varphi}^2}{\dot{r}} \right] - \frac{B}{4\Delta} \left[A_r \frac{\dot{\xi}^4}{\dot{r}^2} + 2A_r \frac{\dot{\xi}^3}{\dot{r}} + B_r \dot{\xi}^2 - \frac{C}{c^2} r \dot{\varphi}^2 \right], \\ G^3 &= \frac{1}{r} \dot{r} \dot{\varphi} \end{aligned} \tag{6}$$

where $\Delta = \frac{3}{4} A^2 \left(\frac{\dot{\xi}}{\dot{r}} \right)^4 + AB \left(\frac{\dot{\xi}}{\dot{r}} \right)^3 - \frac{3}{2} A \frac{C}{c^2} \frac{\dot{\xi}}{\dot{r}} - \frac{1}{2} B \frac{C}{c^2}$ and $A_t = \frac{\partial A}{\partial t}$, $A_r = \frac{\partial A}{\partial r}$, $B_t = \frac{\partial B}{\partial t}$, $B_r = \frac{\partial B}{\partial r}$.

Assuming $\frac{\partial^2 \delta r(\tau)}{\partial \tau^2} = -B_c \delta r$ one gets the compressibility after integration (2):

$$\kappa = \kappa'_\tau \Delta t_{ph} \square - \frac{1}{S} \int_{r(t)}^{r(t+\Delta t_{ph})} B_c d^2 r. \tag{7}$$

Here one takes into account that $\frac{\partial \tilde{\pi}}{\partial \tau} = \frac{\partial \tilde{\pi}}{\partial t} \frac{\partial t}{\partial \tau} \square \Delta t_{ph}$. The Berwald curvature B_c is equal to zero everywhere except of the isotherm plateau. Therefore the expression (7) can get the form

$$\kappa \square - \frac{1}{S} \int_{r(t)}^{r(t+\Delta t_{ph})} B_c d^2 r = -\frac{1}{S} \int_{r(0)}^{r(\Delta t_{ph})} \frac{\partial B_c}{\partial \tilde{r}} d^2 r = -(B_c(r(\Delta t_{ph})) - B_c(0)). \tag{8}$$

Here $B_c(0) \equiv B_c(r(0))$ is a constant of the phase transition.

The theoretical dependences B_c on displacement r at $\varphi = 0$ are shown for compression rates $V = 2$ and $V = 10$ in Fig. 1. One can see that $B_c(r)$ has two singularities, position of which depends on the compression rate. At increase of V , the singular points shift to each other, and, respectively, a region $\Delta \tilde{\pi}_{ph}$ of phase transition becomes narrower according to Fig. 1.

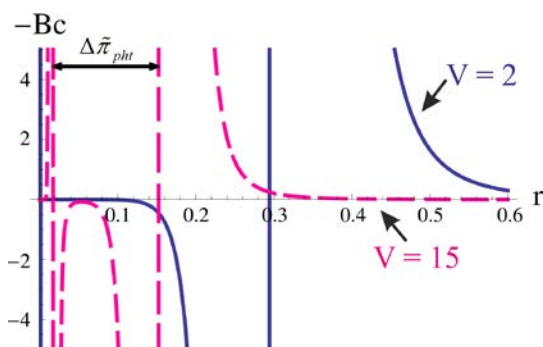


Figure 1. The dependences of Berwald curvature B_c on displacement r for compression rates $V = 2$ (blue solid line) and $V = 10$ (magenta dashed line).

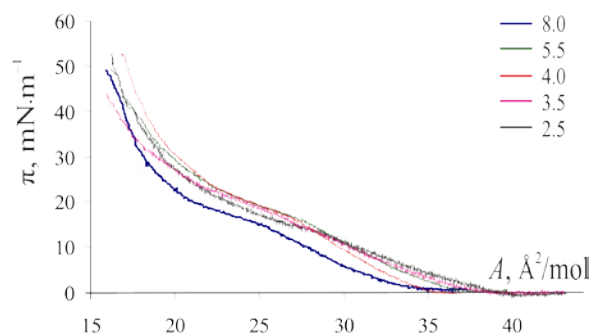


Figure 2. $\tilde{\pi} - A$ isotherms for a stearic acid monolayer formed at compression rates V equal to 8.0 (blue), 5.5 (green), 4.0 (red), 3.5 (magenta), 2.5 mm/min (black).

5. Experimental results and discussion

Typical compression $\tilde{\pi} - A$ isotherms at different compression rates V are shown in Fig. 2. One can see that depending on V , the phase transitions can vary in area per molecule and start at different molecular area A . At low V the surface pressure increases sharper in range of high value A than at high V : the first order phase transition begins at lower A and is smoother (compare isotherm for rates 2.5 and 8.0 mm/min). These isotherms have been used to get the dependences of compressibility on surface pressure according to data processing, described above.

The dependences of compressibility $\kappa(\tilde{\pi})$ on $\tilde{\pi}$ at different compression rates V are represented in Fig. 3. Each of them represents itself three sets of data which correspond to three filtration parameters: $\{n_1 = 6, m_1 = 6\}$, $\{n_1 = 6, m_1 = 7\}$, $\{n_1 = 7, m_1 = 6\}$ for $V = 3.5, 4.0, \text{ and } 5.5$ mm/min (Fig. 3 (b – d)) and

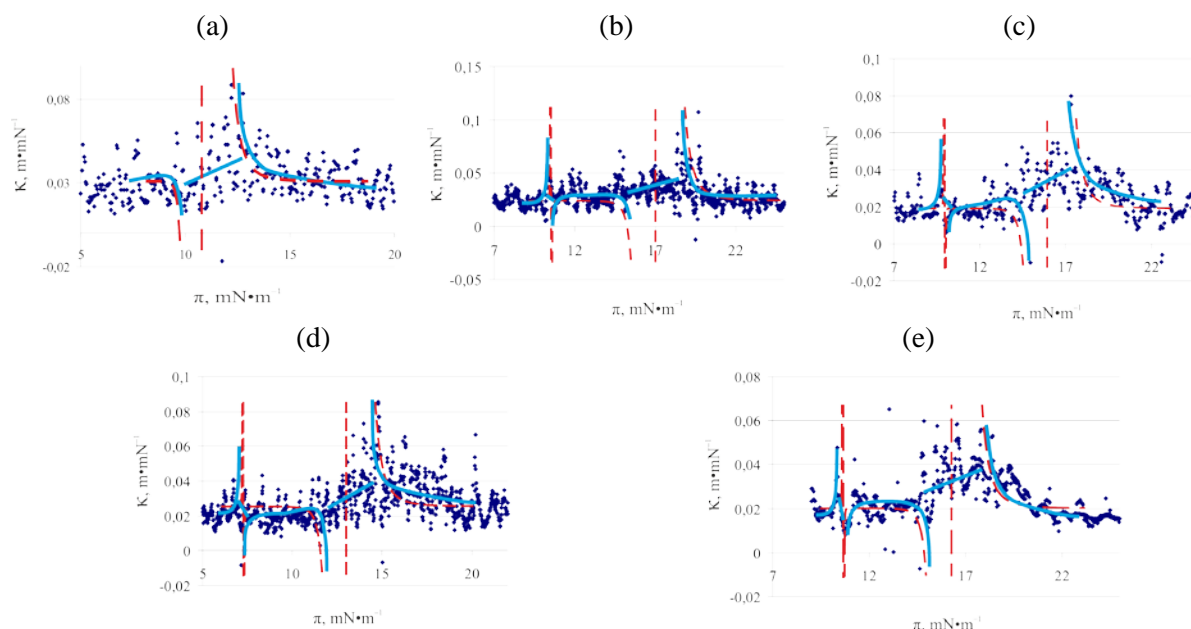


Figure 3. The dependences of the compressibility κ on $\tilde{\pi}$ at the 2D-phase transition of first order in the monolayer at different compression rates: $V = 2.5$ (a), 3.5 (b), 4.0 (c), 5.5 (d), 8.0 mm/min (e). Symbols denote experimental data processing results, solid lines are fitting, dashed lines are the theoretical predictions.

$\{n_1 = 3, m_1=3\}$, $\{n_1 = 4, m_1=5\}$, $\{n_1 = 5, m_1=3\}$ for $V = 8.0$ mm/min (Fig. 3 (e)). One can see that the dependences $\kappa(\tilde{\pi})$ have a complex non-linear character in the region of the first order phase transition.

The experimental dependences of compressibility κ on surface pressure $\tilde{\pi}$ for the stearic acid monolayer at different compression rates V have been approximated by the theoretical curves (8), red dashed lines in Fig. 3. As one can see the theoretical curves elucidate the origin of dispersion of compressibility. The phase transition width $\Delta\tilde{\pi}_{pht}$ was defined as a difference between two singular points on a theoretical curve in Fig. 1. Table 1 demonstrates that $\Delta\tilde{\pi}_{pht}$ is a function of the compression rate V . The phase transition width was found out to decrease with the increasing of the compression rate that is in accordance with our theoretical results shown in Fig. 1.

Table 1. The value of phase transition width $\Delta\tilde{\pi}_{pht}$ at different compression rates V .

V , mm/min	$\Delta\tilde{\pi}_{pht}$, mN/m
2.5	-
3.5	6.5
4.0	6.0
5.5	5.7
8.0	5.5

6. Conclusion

Thus, the approach has been proposed that allows to examine the anomalous behavior of compressibility at 2D phase transition of first order. The proposed approach is used to describe the formation of Langmuir stearic acid monolayers.

References

- [1] Motschmann H, Möhwald H 2001 *Langmuir–Blodgett Films*. In: *Handbook of Applied Surface and Colloid Chemistry*. Ed. Holmberg K (John Wiley & Sons, Ltd)
- [2] Fiore C E, Carneiro C E I 2008 *ArXiv [cond-mat.stat-mech]* 0809.4023v1
- [3] Modlińska A, Bauman D 2011 *Int. J. Mol. Sci.* **12** 4923
- [4] Toma L M, Gengler R Y N, Prinsen E B, Gournis D, Rudolf P 2010 *Phys. Chem. Chem. Phys.* **12** 12188
- [5] Bhande R S, Landge Y A, Giri P 2012 *J. Chem. Pharm. Res.* **4(6)** 3297
- [6] Balan V, Grushevskaya G, Krylova N, Neagu M, Oana A 2013 *Applied Sciences* **15** 30
- [7] Grushevskaja G V, Krylova N G 2011 *Hypercomplex Numbers in Geometry and Physics* **15** 128 (In Russian)
- [8] Neagu M, Krylova N G, Grushevskaya H V 2013 *J. Math. Phys.* **54** 031508
- [9] Grushevskaya H V, Lipnevich I V, Orekhovskaya T I 2013 *J. Mod. Phys.* **4** 7
- [10] Landau L D, Lifshits E M 1982 *Electrodynamics of continuous media*. In: *Theoretical Physics*. Vol. 8 (Moscow: Science)
- [11] Bao D, Chern S, Shen Z 2000 *An Introduction to Riemann-Finsler Geometry* (Berlin: Springer)