Multiple-relaxation-time Finsler-Lagrange dynamics in a compressed Langmuir monolayer

V. Balan

University Politehnica of Bucharest, Faculty of Applied Sciences,
Department of Mathematics-Informatics,
313 Splaiul Independentei, 060042 Bucharest, ROMANIA.

H. V. Grushevskaya and N. G. Krylova

Physics Department, Belarusian State University,
4 Nezavisimosti ave., 220030 Minsk, BELARUS

M. Neagu

Department of Mathematics and Informatics, University Transilvania of Brașov,
50 Iuliu Maniu Blvd., 500091 Brașov, ROMANIA

(Dated:)

In this paper an information geometric approach has been proposed to describe the two-dimensional (2d) phase transition of the first order in a monomolecular layer (monolayer) of amphiphilic molecules deposited on air/water interface. The structurization of the monolayer was simulated as an entropy evolution of a statistical set of microscopic states with a large number of relaxation times. The electrocapillary forces are considered as information constraints on the statistical manifold. The solution curves of Euler-Lagrange equations and the Jacobi field equations point out contracting pencils of geodesic trajectories on the statistical manifold, which may change into spreading ones, and converse. It was shown that the information geometrodynamics of the first-order phase transition in the Langmuir monolayer finds an appropriate realization within the Finsler-Lagrange framework.
Mathematics Subject Classification (2010): 53B40, 53C80, 81T13.

Keywords: Berwald-Lagrange curvature; flag curvature; first-order phase transition; Langmuir monolayer; statistical manifold.

I. INTRODUCTION

The relaxation processes, which depend on their flowing-speed $V$ are experimentally observed during phase transitions from an isotropic phase to anisotropic 2d-phases or to a 3d-phase (collapse state) of compressed monolayers fabricated from amphiphilic molecules of surface-active substances. We call isotropic phase a liquid-expanded (LE) state. The tilted liquid condensed (LC) states $L_2$, $L'_2$, $Ov$, and $S$ are related to the anisotropic 2d-phases with slant hydrophobic "tails" (hydrophobic moiety) of the amphiphilic molecules. The untilted solid-like anisotropic 2d-phases $L''_2$ and $CS$ are called solid condensed (SC) states [1, 2]. The compressed monolayers from hydrated surface-active substances extracted from biological membranes crystallize at low compression rates $V$ [3, 4] and collapse during quasi-static compression. Such Langmuir monolayers become metastable and do not collapse at much higher surface pressures when compressed faster than a threshold rate, while the dependence of monolayer properties on the compression rate is not determined by the composition of the monolayer and, respectively, by different miscibilities of substances [5]. This metastable state is a state of type of supercooled liquid in the first-order phase transition [6]. The properties of metastable state depend on the action time, similarly to the glass or ferroelectric cases. A system can stay arbitrarily long in the supercooled liquid state, if the seed crystallizing centers are absent. Such centers are imperfections, or impurity particles, or new phase elements of the above-critical size. A supercooled-liquid heterogeneous dynamics is a dynamics of a system consisting from individual relaxing units which have site-specific relaxation times and, hence, are characterized by different coexisting timescales [7]. Similar multiple-relaxation-times heterogeneous dynamics depending on compression speed holds in a Langmuir film of gold nanoparticles with diameter less than 7 nm, because there exist effects of the speed on the compression process, such as a non-linear dependence of the loss absolute value (the product between the viscosity of the Langmuir monolayer and the compression rate $V$) and the loss factor on $V$ [8].

The Langmuir monolayer structure is formed from hydrate complexes of surfactant, be-
cause a water subphase abundance is expelled from compressed monolayer to outside. This process is revealed as the occurrence of water drops on the side of hydrophobic tails. These drops were observed as hill-like structures when the tilted LC 2d-phases or the untilted SC are formed. The tails in the tilted phases are not arranged vertically, and because of that, unlike the case of untilted phases, the hydrophobic interactions prevent the return of expelled water. This ejection process depends on the speed \( V \) of monolayer compression. The drops of ejected subphase particles were also observed as subsided bubbles in ultra-thin Langmuir-Blodgett (LB) films. If the LB-film is thick (9 and more monolayers), the water from the bubbles is retained via interlayer interactions and the bubbles do not fall. The dependence of hydrate-complex stability on the compression speed \( V \) for a monolayer formed from polymers such as Isotactic and Syndiotactic Poly(methyl methacrylate) at a dilute state can explain the dependence of the blending ratio on \( V \), which was observed in [11]. These substances - being miscible at the rates \( V \sim 0.001 \text{ mm/s} \) - are not miscible if \( V = 0 \). The width of the plateau of isotherms for stearic acid also depends on the value of the compression rate \( V \). The most commonly used recent models of phase transitions in layered systems are the statistical lattice models. Such an approach is based upon mean-field theory. The phase nuclei (phase elements, relaxing units) may appear/disappear with a given probability at each lattice location, when the monolayers are structuring. These phase elements have their own lifetimes (relaxation times). A theory of 2d-phase transitions was developed for a model of interacting tails of amphiphilic molecules, where electrostatic repulsion of polar "heads" (hydrophilic moiety) of these molecules is considered as a small perturbation. In this theory, the free energy is varied under the assumption of homogeneity of the phase elements, and one completely neglects the existence of the metastable transient state. Besides this, the head-enveloping water molecules, whose number depends on the geometry at certain area per molecule, play a crucial role for the overall electric properties of the monolayer. The free energy of a system with such a feature - like the presence of a broad spectrum of relaxation times of heterogeneous phase elements, that is characteristic for the metastable state - is also varied in the Kolmogorov-Mehl-Johnson-Avrami approach to the first-order phase transition. This approach, however, does not give any information about the transient phase-element kinetics. Since the metastable state is an unstable one with a negative compressibility, it can be represented as a collection of a large number of elementary unstable independently
relaxing units, for example, bistable elements in a Preisach model [24–26]. The use of the Preisach model, which was initially proposed to describe the ferromagnetic case, allows to take into account an entropy contribution, which is due to the random polarization of the environment, as “coercive forces” and, respectively, gives a statistical distribution of relaxation times. However, it was shown in [27], that an appropriate description of the metastable state is impossible without variation of the entropy contribution, particularly, without variation of the coercive forces in the Preisach model.

The evolution of a discrete set of molecule orientation parameters, which describe the crystal space rearrangement, is examined in the hydro-dynamic (continuous) limit of a kinetic theory of the second-order phase transition from the tilted allotropic crystalline form to the untitled one [19]. Then, the powerful field theory and the renormalization group methods are used to describe the second-order phase transitions. The continuous parameterizations with space-scaling are not applicable for first-order phase transitions, because the metastable state has to be scaled in the time domain, but not in the space one [28].

The first-order phase transition in Langmuir monolayers - as process with relaxation-time dispersion - is characterized by a statistical distribution, that is fluctuated between the statistical distributions \( p_L \) and \( p_S \) for amphiphilic molecules in the expanded liquid and in the crystalline phases, respectively. We shall further use the information geometrodynamics [29–33] and shall variate the entropy in order to describe the 2d-phase transition of the first order. The information geometric techniques will be utilized to analyze the stability of the most probable trajectories on the statistical manifold, which consists of the set of probability distributions \( \{ p_i \} \) for the \( i \)-th microscopic states (microstates) under certain thermodynamic conditions regarded as information constrains. The statistical manifolds can be non-trivial tangent bundles [34]. The dependence of the structurization process in the Langmuir monolayers on the compression rate means that an addition of compression-velocity vector to a tangent space of the monolayer may change the sub-spaces formed by sets of tangent vectors at points of the arbitrary trajectory in the coordinate space of the monolayer. Then, there exists a non-trivial slice made of tangent unit vectors, which form the so-called indicatrix surface over the (base) coordinate space. Accordingly, a heterogeneous dynamics of the structurization occurs in the tangent bundle. Therefore, in our paper we will use Finsler geometry structures [35–37] of tangent bundles to describe the Langmuir monolayer structurization as a process that is characterized by a dynamic scaling law for
the relaxation times and by the presence of a distribution of timescales.

The goal of this article is to construct a statistical manifold of compressed monolayers, which are deposited on the air/water interface, and the geometrodynamics of this manifold, and to study the structurizing monolayers in transient state of the first-order phase transition.

II. THE STATISTICAL MANIFOLD FOR FIRST-ORDER 2D-PHASE TRANSITIONS

We assume that the phase nuclei (phase elements) in Langmuir monolayers are amphiphilic molecules in two states: the hydrated complexes and the molecules leaving the complexes (in a free state). A microstate introduced as the phase element of the 2d-membrane is a continuous analog of a phase nucleus from the ordinary theory of the first-order phase transitions. An evolution of macroscopic states (macrostates) in the first-order 2d-phase transition is a decreasing (increasing) surface tension due to the decay (production) of the phase elements in a compressed Langmuir monolayer.

In order to obtain the differential equations which describe the dynamics of the system on the statistical manifold, we shall use the maximum entropy principle [29] and the maximum entropy production principle [30, 31] in the form proposed in [32]. Let us consider the distribution \( p(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; t), N \to \infty \) for \( N \) microstates (\( N \) phase-elements) with the coordinates \( \{\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N\} \) and the eigenfrequencies \( \{\omega_1, \omega_2, \ldots, \omega_N\}, N \to \infty \). These \( N \) microstates arise at the moments \( t_i, i = 1, \ldots, N \) and decay during the periods \( \Delta t_i, i = 1, \ldots, N \) with relaxation times \( \{\tau_1, \tau_2, \ldots, \tau_N\} \). Therefore, one has to replace the probability distribution \( p(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; t) \) with the following expression:

\[
p(\vec{r}_1, t_1 + \Delta t_1; \vec{r}_2, t_2 + \Delta t_2; \ldots, \vec{r}_N, t_N + \Delta t_N), N \to \infty.
\]

The evolution of entropy \( S \) reads

\[
S(t_i + \Delta t_i) - S(t_i) = - \int p(\vec{r}_1, t_1 + \Delta t_1; \vec{r}_2, t_2 + \Delta t_2; \ldots, \vec{r}_N, t_N + \Delta t_N) \times \ln \frac{p(\vec{r}_1, t_1 + \Delta t_1; \vec{r}_2, t_2 + \Delta t_2; \ldots, \vec{r}_N, t_N + \Delta t_N)}{p(\vec{r}_1, t + \Delta t_1; \ldots; \vec{r}_i, t_i; \ldots, \vec{r}_N, t_N + \Delta t_N)} d\vec{r}_1 \ldots d\vec{r}_N. \tag{II.1}
\]
Here the entropy $S(t_i + \Delta t_i)$ and $S(t_i)$ at the moments $t_i + \Delta t_i$ and $t_i$, respectively, are defined as

\[
S(t_i + \Delta t_i) = S \left( p(\vec{r}_1, t_1 + \Delta t_1; \ldots ; \vec{r}_i, t_i + \Delta t_i; \ldots ; \vec{r}_N, t_N + \Delta t_N) \right),
\]

(II.2)

\[
S(t_i) = S \left( p(\vec{r}_1, t_1 + \Delta t_1; \ldots ; \vec{r}_{i-1}, t_{i-1} + \Delta t_{i-1}; \vec{r}_i, t_i; \vec{r}_{i+1}, t_{i+1} + \Delta t_{i+1}; \ldots ; \vec{r}_N, t_N + \Delta t_N) \right).
\]

(II.3)

An information about the macrostate imposes constraints on the distribution of the microstates. This additional information is an increment $\Delta U_i$ of the 2d-membrane free energy $U_s$ for the $i$-th phase element of the membrane, due to the change of the electric potential difference on the interface between air and water subphases in electrocapillarity phenomena \[38–41\]. All the relaxation processes for all the $N$ phase elements give a contribution $\Delta U_s$ into $U_s$. Therefore, $\Delta U_s$ is given by the following expression:

\[
\Delta U_s = \sum_{i=1}^{N} \Delta \sigma_i^{electrocap} A_{t_i} \Delta t_i.
\]

(II.4)

Here $\Delta \sigma_i^{electrocap}$ is a surface-tension increment owing to an action of the electrocapillary forces during a small time interval $\Delta t_i$ for $i$-th phase element, $A_{t_i} = \frac{\Delta A}{\Delta t_i} < 0$ is the rate of change of area $A$ per molecule, for the $i$-th phase element. A constraint stipulated by the adding the information (II.4) regarding the macrostate of the system has the following form:

\[
\Delta s \int (H + i \Gamma) p(\vec{r}_1, t_1 + \Delta t_1; \ldots ; \vec{r}_i, t_i + \Delta t_i; \ldots ; \vec{r}_N, t_N + \Delta t_N) dr_1 \ldots dr_N
\]

\[
= - \sum_{i=1}^{N} \Delta \sigma_i^{electrocap} A_{t_i} \Delta t_i,
\]

(II.5)

where $H$ is the Hamiltonian, $\Gamma$ is the damping of the system, and $\Delta s$ is the increment of the evolution parameter $s$. By applying the Laplace transform in the left hand side of the expression (II.5), we can rewrite it as

\[
\Delta s \int (H + i \Gamma) p(\vec{r}_1, t + \Delta t_1; \ldots ; \vec{r}_i, t + \Delta t_i; \ldots ; \vec{r}_N, t + \Delta t_N) dr_1 \ldots dr_N
\]

\[
= \Delta s \sum_{i=1}^{N} \int (\omega_i + i \tau_i^{-1}) p(\vec{r}_1(\omega_1), \ldots ; \vec{r}_i(\omega_i), \ldots ; \vec{r}_N(\omega_N)) dr_1(\omega_1) \ldots dr_N(\omega_N)
\]

\[
= - \sum_{i=1}^{N} \Delta \sigma_i^{electrocap} A_{t_i} \Delta t_i.
\]

(II.6)
Since the relations $\omega_i \tau_i \gg 1$, $N \to \infty$ hold for the phase transition of the first order, by using the expression (II.6) and the normalization condition

$$
\int p(\vec{r}_1(\omega_1), \ldots, \vec{r}_i(\omega_i), \ldots, \vec{r}_N(\omega_N)) \, dr_1(\omega_1) \ldots dr_N(\omega_N) = 1, 
$$

one gets the relaxation times $\tau_i$, $i = 1, \ldots, N$:

$$
\tau_i = -\frac{\Delta t_i}{\Delta s}.
$$

By varying (II.1) jointly with the constraints (II.6) and (II.7) multiplied with the Lagrange multipliers $\lambda_1$ and $\lambda_2$, respectively, we find a non-stationary statistical distribution to which our system evolves during the time interval $\Delta t_i$:

$$
p(\vec{r}_1, t_1 + \Delta t_1; \ldots; \vec{r}_i, t_i + \Delta t_i; \ldots; \vec{r}_N, t_N + \Delta t_N)
$$

$$
= p(\vec{r}_1, t_1 + \Delta t_1; \ldots; \vec{r}_{i-1}, t_{i-1} + \Delta t_{i-1}; \vec{r}_i, t_i; \vec{r}_{i+2}, t_{i+2} + \Delta t_{i+2}; \ldots; \vec{r}_N, t_N + \Delta t_N)
$$

$$
\times \frac{e^{\Delta s \lambda_2(\omega_i + i \tau_i^{-1})}}{Z_i},
$$

where $Z_i$ is the statistical sum

$$
Z_i = \int e^{\Delta s \lambda_2(\omega_i + i \tau_i^{-1})}
$$

$$
\times p(\vec{r}_1, t_1 + \Delta t_1; \ldots; \vec{r}_{i-1}, t_{i-1} + \Delta t_{i-1}; \vec{r}_i, t_i; \vec{r}_{i+2}, t_{i+2} + \Delta t_{i+2}; \ldots; \vec{r}_N, t_N + \Delta t_N) \, dr_i.
$$

Hence, one can determine the statistical manifold $\mathcal{M}$ of the examined system with the given set of relaxation times (II.8) regarded as a set of probabilities (II.9):

$$
\mathcal{M} = \{p(\vec{r}_1(\tilde{t}_1), \ldots, \vec{r}_i(\tilde{t}_{i-1}), \vec{r}_i(t_i), \vec{r}_i(\tilde{t}_{i+1}), \ldots, \vec{r}_N(\tilde{t}_N)) e^{\Delta s \lambda_2(\omega_i + i \tau_i^{-1})}/Z_i\},
$$

where $\tilde{t}_i = t_i + \Delta t_i$, $i = 1, \ldots, N$.

Let us suppose that $\sum_{i=1}^N \Delta t_i$ be equal to a phase-transition time $T_{pht}$:

$$
\sum_{i=1}^N \Delta t_i = T_{pht}.
$$

According to the expressions (II.8) and (II.12), the value of the parameter $s$ is defined by the phase-transition time $T_{pht}$ as: $\Delta s = -\frac{T_{pht}}{\sum_{i=1}^N \tau_i}$. Then, assuming that $\lambda_2 = \sum_{i=1}^N \tau_i$ and performing subsequent iterations of the type described in (II.9), we eventually find the
distribution function during the phase transition, e.g., from the liquid expanded state with the distribution function \(p_L\) to the crystalline condensed one with the distribution function \(p_{CS}\):

\[
p_{CS}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; t + T_{ph}) = p_L(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; t) \frac{e^{-(H+i\Gamma)T_{ph}}}{Z},
\]

(II.13)

where the statistical sum \(Z\) is defined by the expression:

\[
Z = \int \prod_{i=1}^{N} dr_i p_L(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; t) e^{-T_{ph}(H+i\Gamma)}.
\]

III. INFORMATION GEOMETRODYNAMICS OF THE STATISTICAL MANIFOLD

By using (II.9), we will construct the geometrodynamic approach with the electrocapillary forces regarded as information constraints to describe the first-order 2d-phase transition in the compressed Langmuir monolayer. The electrocapillary part of free energy (II.4) is determined by the following Lagrange function \[42]\:

\[
L(t, r, \dot{r}, \dot{\varphi}) = \frac{m}{2} \dot{r}^2 + \frac{mr^2 \dot{\varphi}^2}{2} - \frac{\tilde{p} r^5 |V|^2}{2} \cdot \dot{r}^{-1} + U(t, r),
\]

(III.1)

where \(m\) is the mass of the particle, \(V\) is the compression speed, \(\tilde{p} = \frac{\pi^2 \sigma^2 \rho_0^2}{R_0^6}\) is a constant which depends on the molecular parameters of the monolayer; \(U_s(t, r)\) is the potential of the electrocapillary forces:

\[
U(t, r) = \tilde{p} \left\{ \left[ -\frac{4}{3} r^5 + \frac{16}{15} (|V| t)^4 + \frac{1}{30} (|V| t)^2 r^3 + \frac{1}{45} (|V| t)^3 r^2 
\right. \right.
\]

\[
\left. + \frac{1}{45} (|V| t)^4 r + \frac{2}{45} (|V| t)^5 \right] e^{\frac{2|V| t}{r}} - \frac{4}{45} \left( \frac{|V| t}{r} \right) \right\} Ei \left( \frac{2|V| t}{r} \right),
\]

(III.2)

and \(Ei = -\int_{-\infty}^{\infty} \frac{e^{t}}{t} dt\) is a special function.

Then, one can reconsider the statistical manifold \(\mathcal{M}\) (II.11), as

\[
\mathcal{M} = \{ p(\vec{r}_1, t_1 + \Delta t_1; \vec{r}_2, t_2 + \Delta t_2; \ldots; \vec{r}_N, t_N + \Delta t_N | \langle \omega_i \tau_i \rangle \propto L_i \Delta t_i / \Delta s, \tau_i = -\Delta t_i / \Delta s) \},
\]

(III.3)

where \(L_i \equiv L(t_i, r_i, \dot{r}_i, \dot{\varphi}_i)\).
Each microstate is a point on the geodesics of the statistical manifold $M$ (III.3), which are parameterized by the macrostates $L_i \tau_i$. The time set $\{t_k, \Delta t_m\}$ determines an $N^2$-dimensional macroscopic vector $\Theta$ with statistical coordinates $\{\theta_{k}^{(m)}\}$, where $k = 1, 2, \ldots, N$ label the microstates and $m = 1, 2, \ldots, N$ enumerate the information constraints. According to the expressions (II.1) and (III.3), the variation of entropy $\delta S$ is determined by the following expression:

$$\delta S = \sum_{a} \left[ \int \ln p(X) \frac{\partial p(X)}{\partial \Delta t_a} \delta(\Delta t_a) dX + \int p(X) \frac{\partial \ln p(X)}{\partial \Delta t_a} \delta(\Delta t_a) dX \right], \quad (\text{III.4})$$

where $X = \{\vec{r}_1(\tilde{t}_1), \ldots, \vec{r}_N(\tilde{t}_N)\}$ is a configuration.

By substituting the expression (II.13) into the equation (III.5) and taking into account (III.3), one obtains the variation of entropy for the Langmuir monolayer in the phase transition:

$$\delta S = \sum_{a} \tau_a \delta s \int p(X) \left[ (H + i\Gamma) - P(X) \dot{X} \right] dX. \quad (\text{III.5})$$

By introducing generalized momenta $P(X)$ and generalized velocities $\dot{X}$ on $M$, by using the relation $P \dot{X} = T_{pht}(H + i\Gamma)^2$ one can rewrite (III.5) in the following form:

$$\delta S = \sum_{a} \tau_a \delta s \int p(X) \left[ (H + i\Gamma) - P(X) \dot{X} \right] dX. \quad (\text{III.6})$$

According to the expressions (III.3), (III.4), and (III.6), the length $\Delta l$ of the configuration (path, trajectory) in the statistical manifold

$$M = \{X| \sum_{i} p_{X_i}(H_i + \Gamma_i) \propto \sum_{i} L_i \Delta t_i / \Delta s, \tau_i = -\Delta t_i / \Delta s \}$$

is determined by the following expression:

$$\Delta l \propto -\sum_{i=1}^{N} L_i \Delta t_i. \quad (\text{III.7})$$

The variation condition $\delta S = 0$ gives us a state with maximum entropy, and hence the solution curves of the Euler-Lagrange equations with the Lagrangian $L_i$ entering in (III.7) is a most probable path on $M$.

Now we can pass to the continuous-medium limit by replacing the finite decrement of the variables in (II.8) with the following differentials:

$$\dot{\xi}_s = \frac{\partial t}{\partial s} = \lim_{\Delta s \to 0} \frac{\Delta t}{\Delta s}.$$
At the continuous limit (III.8), the expression (III.7) becomes the action

$$\Delta l \propto - \int L \dot{\xi}_s ds$$

(III.9)
on the statistical manifold $M$, with the metric function $dl$:

$$dl \propto - L \dot{\xi}_s ds.$$  (III.10)

IV. THE FINSLER-LAGRANGE DYNAMICS OF THE LANGMUIR MONOLAYER: NUMERICAL MODELING

Let us assume that all the phase elements decay with the relaxation time $\dot{\xi}_s = 1$ during a small time-interval. In this case, the information geomerodynamics of the particles from the compressed monolayer during small time-intervals is described by the action (III.10) with $s = t$. Therefore the Finsler-Lagrange space of the monolayer in polar coordinates $(r, \varphi)$ can be described by the following non-relativistic action

$$dl = mc^2 dt - L dt,$$  (IV.1)

where $L$ is the Lagrange function (III.1). Now, one can get the 2-dimensional most probable trajectory (mean trajectory) of the particle in the monolayer. By making zero the variation of the action (IV.1), one obtains the following system of differential equations for geodesics (the Euler-Lagrange equations):

$$\frac{dy_1}{dt} + 2G_{(1)1}(t, x^k, y_1^k) = 0, \quad \frac{dx^k}{dt} = \dot{x}^k \equiv y_1^k,$$  (IV.2)

where

$$G_{(1)1}^{(1)} = \frac{\tilde{p}r^3 |V| e^{\frac{2iv}{r}} (5r \tilde{r}^{-1} - 2|V| \tilde{r}^{-1} + |V| r \tilde{r}^{-2}) - \frac{1}{2} \frac{\partial U}{\partial r} - \frac{mr}{2} \dot{\varphi}^2}{m - 2\tilde{p}r^5 |V| e^{\frac{2iv}{r}}, \dot{r}^{-3}}.$$

$$G_{(1)1}^{(2)} = \frac{\tilde{r}}{r} \dot{\varphi}.$$

(IV.3)

Now we shall show that the compression speed $V$ of the monolayer determines the magnitude of cohesive force (friction), which acts on the monolayer moving on the subphase surface. If $V = 0$, then the system of differential equations (IV.2) (IV.3) reduces to:

$$-r \dot{\varphi}^2 + 20\tilde{p}r^4/3m + \ddot{r} = 0, \quad 2 \dot{\varphi} \dot{r} + \varphi = 0.$$  (IV.4)
Since $V = 0$, a solution of the equation (IV.4) is a most probable trajectory in absence of friction. In this case, the monolayer is a conservative system. The shape of geodesic trajectories (IV.4) from Fig. 1a shows that the molecules of the monolayer in average move around the reference point, along the extended orbits revolved to each other, and periodically pass from one orbit to another. Thus, if $V = 0$, the molecules remain in the hydrated complex, and the system behaves itself like a conservative one.

According to Fig. 1b, the monolayer - compressed at small $V$ - may be represented as a system with a weak dissipation and, respectively, the trajectories are of limit-cycle type. A mean trajectory of the particle for large $V$ exhibits inflexion points, as shown in Fig. 1c. For this reason, such paths may describe metastable states of the system in the first-order phase transition. We shall further investigate the structure of the set of inflexion points,

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{The mean trajectories $\vec{r}$ of the particle in the compressed monolayer at $\tilde{p} = 10$, $m = 1$ for different compression speeds: (a) $V = 0$; (b) $V = 1$; (c) $V = 500$.}
\end{figure}

in the sense of Jacobi stability by means of the KCC (Kosambi-Cartan-Chern) invariants theory [35].
V. JACOBI EQUATIONS FOR DEVIATIONS OF GEODESICS FROM AN INSTANTON-LIKE GEODESIC

A system of differential equations for the variation \((\delta r, \delta \varphi)\) (which describe Jacobi fields) of the geodesics satisfying the system (IV.2) has the following form [42]:

\[
\ddot{\delta r} = \frac{\ddot{p}r}{45r^3(2\ddot{p}Vr^5e^{2\varphi} + m\varphi^3)} \left(8V^6\varphi^6Ei \left(\frac{2V^t}{r}\right)\right) \dot{r}^2 \delta r + e^{2\varphi}r(45Vr^5(5r - 2Vt)\delta r - \delta r(4V^5t^5 + 2V^4t^4r + 182V^3t^3r^2 - 807V^2t^2r^3 + 1536Vtr^4 - 1200r^5)\dot{r}^2)), \quad (V.1)
\]

\[
\delta \ddot{\varphi} = 0. \quad (V.2)
\]

In order to study the Jacobi stability, one can assume that the trajectory with inflexion points from Fig. 1c is located in the vicinity of an instanton-like geodesic. A system of differential equations for the instanton-like geodesic has the following form [42]:

\[
\dot{r}^3 + 6\ddot{p}V \frac{r^5e^{2\varphi}}{m} = 0, \quad \varphi - C_0/r = 0, \quad (V.3)
\]

where \(C_0\) is a constant. To obtain a solution of the system (V.3) for large enough compression-times, one can simplify the system, by taking into account that \(r \to (R_0 - Vt)\) for \(t \to \infty\). Then the system (V.3) takes a following form:

\[
\dot{r}^3 + 6\ddot{p}V \frac{r^5e^{2\varphi}}{m} = 0, \quad \varphi - C_0/r = 0, \quad (V.4)
\]

a solution of which is

\[
\begin{align*}
r &= 27m^2\ddot{p}R_0Ve^{-\frac{Vt}{R_0 - Vt}} \\
&\times \left\{ \left( \frac{6\ddot{p}R_0}{R_0 - Vt} + 9m^3V^3 \right) e^{-\frac{2}{3}\frac{Vt}{R_0 - Vt}} - 6\ddot{p}R_0 \left( -R_0 - Vt \right) + 4 \cdot 6\ddot{p}R_0 e^{-\frac{2}{3}\frac{R_0}{R_0 - Vt}} \right\}^{-1} \\
&\quad \times \left( Ei \left( \frac{2}{3} \right) + Ei \left( \frac{2R_0}{3(R_0 - Vt)} \right) \right) \quad (V.5)
\end{align*}
\]

Taking into account the expression (V.3), a solution of the system (V.1, V.2) gives a mean trajectory \((r(t) + \delta r(t), \varphi(t) + \delta \varphi(t))\) of motion for a particle in the monolayer. A result of the numerical calculation of the Jacobi fields is presented in Fig. 2 in Cartesian coordinates \((x(t), y(t))\). The solution shows that the contraction of pencils of geodesic trajectories on the statistical manifold interchanges by spreading, and converse.

The curvature \(K\) in the coordinate space for the trajectory \((x(t), y(t))\) can be defined by the following formula [43]:

\[
K(t) = \frac{\dot{x}\ddot{y} - \dot{y}\ddot{x}}{(\dot{x}^2 + \dot{y}^2)^{3/2}}. \quad (V.6)
\]
The dependence of the curvature $K(t)$ on the time $t$ is represented in Fig. 3a. The four insets into this figure illustrate scale-invariant fragments of the dependence of $K(t)$, which reveal its fractal-like behavior. One then may examine a set of states with null curvatures $K$ and, respectively, a practically infinite number of inflexion points of the curve, at sufficiently large times. The infinite number of inflexion points implies the coexistence of liquid-expanded and crystalline phases. Hence, the monolayer is in a metastable state during the first-order phase transition. We further calculate the Lagrange-Berwald curvature $K_B$ on the tangent bundle, which is a natural Lagrangian extension $K$ of the flag curvature from Finsler space theory (see [44, p. 54]). The flag curvature $K_B$ of the monolayer is determined by the following formula [45]:

$$K_B := K(t, r, \varphi, \dot{r}, \dot{\varphi}; X) \overset{\text{def}}{=} \frac{B_{hijk}y^h_1X^i_1y^j_1X^k}{(g_{hj}g_{ik} - g_{hk}g_{ij})y^h_1X^i_1y^j_1X^k}, \quad (V.7)$$

considered with respect to the vector field $X$:

$$X(t, r, \varphi) = X^1 \frac{\partial}{\partial r} + X^2 \frac{\partial}{\partial \varphi} \neq 0,$$
FIG. 3: Time dependence of curvature $K$ (a) and of flag curvature $K_B$ (b). Four insets into figure a illustrate a scale-invariant behavior of the curvature $K$.

where $B_{hijk} = g_{hs} \frac{\partial^3 G}{\partial y_i \partial y_j \partial y_k^h}$. The flag curvature $K_B$ along the trajectory $\tilde{r} = \tilde{r} + \delta \tilde{r}$ with the radial flag

$$\{\tilde{y}_1, X\} = \{\tilde{y}_1, (X^1, 0)\}, \quad \tilde{y}_1 = (\dot{\tilde{r}}_0, \dot{\phi}) = (\dot{r} + \delta \dot{r}, \dot{\phi} + \delta \dot{\phi})$$

is equal to

$$K_B = \left[ \frac{18}{\tilde{r}^6 |V| e^{-3\sqrt{\tilde{r}}} \frac{4U(t, \tilde{r})}{m\tilde{r}^2 \dot{\phi}^2}} \right] \cdot \dot{\tilde{r}}^2 \quad (V.8)$$

The result of the calculation of $K_B$ (V.8) is represented in Fig. 3b. By comparing figures 3a and 3b, we conclude that $K_B$ becomes non-positive earlier than the curvature $K$ does. Thus, the loss of stability of the monolayer state begins with the change of sign of the flag curvature $K_B$ and leads to a fractal-like distribution of phase elements in the monolayer space. After the phase transition was accomplished, the fractal time structure within the monolayer is maintained during a certain time interval.
VI. DISCUSSION AND CONCLUSIONS

By using the thermodynamics of non-stationary processes, we describe an entropy evolution of microstates, and determine a statistical manifold, on which a multiple-relaxation-time dynamics occurs. We propose a continuous parameterization of the first-order phase transition (a heterogeneous dynamics) for compressed monolayers of amphiphilic molecules on which the electrocapillary forces act. The information geometrodynamic approach with the electrocapillary forces regarded as an information constraint is then applied to describe the phase transition from a liquid expanded state into a tilted condensed state with a time fractality for the monolayers. The self-similarity of ordinary coordinate curvature $K$ is an appearance of the time scaling for arbitrary time domain.

The flag curvature $K_B$ of the tangent bundle changes its sign from $''+''$ to $''-''$ already at small compression times, when the apparent $K$ still is positive. The negative $K_B$ and, respectively, the non-stability of hydrated complexes in a compressed monolayer leads to an escape of water molecules from the complex, resulting in the disappearing of steric hindrances to interact amphiphilic molecules each other. Therefore, the phenomenon of precise miscibility of blended Langmuir monolayer [11], that is fabricated from apparently immiscible substances may proceed from the non-stability.

Hence, the Finsler geometry approach allows to analyze the structural stability loss, leading to structuring of transient processes in compressed monolayers.

VII. ACKNOWLEDGEMENTS

The present work was developed under the auspices of the Project RA-4.2 /14.06.2014 - BRFFR-RA F14RA-006, within the cooperation framework between Romanian Academy and Belarusian Republican Foundation for Fundamental Research.

[1] D. Andelman, F. Brochard, C. Knobler and F. Rondelez, ”Structures and phase transitions in Langmuir monolayers”, In: Micelles, Membranes, Microemulsions and Monolayers (Springer, Heidelberg, 1994), pp. 559–602.
[2] A. Tadjer, A. Ivanova, Y. Velkov, S. Tzvetanov, M. Gotsev and B. Radoev, "Exploratory study of dielectric properties of insoluble monolayers: molecular models", Int. J. Quantum Chemistry 107, 1719-1735 (2007).

[3] A.D. Postle, E.L. Heeley and D.C. Wilton, "A comparison of the molecular species compositions of mammalian lung surfactant phospholipids", Comp. Biochem. Physiol. A: Mol. Integr. Physiol. 129, 65-73 (2001).

[4] M. Eeman and M. Deleu, "From biological membranes to biomimetic model membranes", Biotechnol. Agron. Soc. Environ. 14(4), 719–736 (2010).

[5] E.C. Smith, J.M. Crane, T.G. Laderas and S.B. Hall, "Metastability of a supercompressed fluid monolayer", Biophysical Journal 85(5), 3048-3057 (2003).

[6] L.D. Landau and E.M. Lifshits, Generation of nuclei at phase transitions, In: Statistical Physics, part 1 (Science, Moscow, 1976), pp.579–582.

[7] R. Richert, "Heterogeneous dynamics in liquids: fluctuations in space and time", J. Phys.: Condens. Matter 14, R703-R738 (2002).

[8] D. Orsi, G. Baldi, P. Cicuta and L. Cristofolini, "On the relation between hierarchical morphology and mechanical properties of a colloidal 2D gel system", Colloids and Surfaces A: Physicochemical and Engineering Aspects 413, 71–77 (2012).

[9] S. Ramos and R. Castillo, "Langmuir monolayers of C17, C19, and C21 fatty acids: textures, phase transitions, and localized oscillations", J. of Chem. Phys. 110, 14, 7021-7030 (1999).

[10] V.M. Anishchik, N.N. Dorozhkin, H.V. Grushevskaya, V.V. Hrushevsky, G.G. Krylov, L.V. Kukharenko and M.A. Senyuk, "Dynamical instability of band structure for Fe-containing nanostructured Langmuir-Blodgett films”, Proc. of SPIE 5219, 141–150 (2007).

[11] N. Aiba, Y. Sasaki and J. Kumaki, "Strong compression rate dependence of phase separation and stereocomplexation between isotactic and syndiotactic poly(methyl methacrylate)s in a Langmuir monolayer observed by atomic force microscopy”, Langmuir 26(15), 12703-12708 (2010).

[12] V.V. Grushevskii and H.V. Krylova, "The thermodynamics of phase states in Langmuir-Blodgett monolayers” (in Russian), In: Low-dimensional systems (Grodnenski Univ., Grodno, Belarus, 2005), pp.30–36.

[13] H.V. Grushevskaya, G.G. Krylov, N.G. Krylova and I.V. Lipnevich, "Modeling of the behavior and statistical analysis of compressibility in the process of Langmuir monolayer structuriza-
17

tion", J. Phys. CS. 643 (2015), 012015.

[14] H.V. Grushevskaya, G. Krylov and V.V. Hrushevsky, "Kinetic theory of phase foliation at formation of Langmuir-Blodgett monolayers", J. Nonlin. Phenom. in Complex Sys. 7, 17–33 (2004).

[15] R.V. Chamberlin, "Non-Arrhenius response of glass-forming liquids", Phys. Rev. B 48, 15638–15645 (1993).

[16] R.V. Chamberlin, "Mesoscopic mean-field theory for supercooled liquids and the glass transition", Phys. Rev. Lett. 82, 2520–2523 (1999).

[17] L.D. Landau and E.M. Lifshits, "Kinetic of first-order phase transition. Nuclei generation", In: Physical Kinetics (Science, Moscow, 1979), pp.503–509.

[18] V.P. Skripov and V.P. Koverda, Spontaneous Crystallization of Overcool Liquids (Science, Moscow, 1984).

[19] V.M. Kaganer, H. M"{o}hwald and P. Dutta, "Structure and phase transitions in Langmuir monolayers", Rev. Mod. Phys. 71, 3, 779–820 (1999).

[20] M. Avrami, "Kinetics of Phase Change", J.Chem. Phys. 7, 1103–1112 (1939); 8, 212–224 (1940); 9, 177–184 (1941).

[21] W. Johnson and R.F. Mehl, "Reaction kinetics in processes of nucleation and growth", Trans. AIME 135, 416–442 (1939).

[22] A.N. Kolmogorov, "To statistical theory of metal crystallization", Izv. Akad. Nauk SSSR, Ser. Matem. 3, 355–359 (1937).

[23] V.Ya. Shur, "Fast polarization reversal process: evolution of ferroelectric domain structure in thin films", In: Ferroelectric Thin Films: Synthesis and Basic Propeties, (Eds.: C.A. Paz de Araujo, J.F. Scott, G.W. Taylor), Ferroelectricity and Related Phenomena Ser., Vol. 10, Chap. 6 (Gordon & Breach Sci. Publ., 1996), pp.153-192.

[24] A.T. Bartic, D.J. Wouters, H.E. Maes, J.T. Rickes and R.M. Waser, "Preisach model for the simulation of ferroelectric capacitors", J.Appl. Phys. 89, 3420–3425 (2001).

[25] L. Cima, E. Laboure and P. Muralt, "Characterization and model of ferroelectrics based on experimental Preisach density", Rev. Sci. Inst. 73, 3546–3552 (2002).

[26] L. Cima and E. Laboure, "Ferroelectric loop modelling based on experimental preisach density determined by FORC method", Ferroelectrics 288, 11–21 (2003).

[27] V.Ya. Shur, I.S. Baturin and E.L. Rumyantsev, "Analysis of the switching data in inhomoge-
neous ferroelectrics”, Ferroelectrics 349, 163-170 (2007).

[28] Sh.-Xi Qu, H. Zheng, A. Barrientos and A. Leyderman, ”Multifractal phase transition in the DavidsonCole relaxation process”, Physics Letters A 268, 360-365 (2000).

[29] E.T. Jaynes, ”Information theory and statistical mechanics 2”, Phys. Rev. 108, 171–190 (1957).

[30] L.M. Martyushev and V.D. Seleznev, ”Maximum entropy production principle in Physics, Chemistry and Biology”, Phys. Reports 426 (2006), 1–45.

[31] A.L. Fradkov and D.S. Shalymov, ”Information entropy dynamics and maximum entropy production principle”, arXiv:1401.2921v1 [cs.IT] 13 Jan 2014.

[32] S.A. Ali, C. Cafaro, A. Giffin and D.-H. Kim, ”Complexity characterization in a probabilistic approach to dynamical systems through information geometry and inductive inference”, Physica Scripta 85, 025009(22pp.) (2012).

[33] S.-I. Amari and H. Nagaoka, Methods of Information Geometry (Oxford University Press and Amer. Math. Soc., 2000).

[34] Zh. Shen, ”Riemann-Finsler geometry with applications to information geometry”, Chinese Annals of Mathematics B 27(1), 73–94 (2006).

[35] P.L. Antonelli and I. Bucataru, ”KCC theory of a system of second order differential equations”, In: Handbook of Finsler Geometry, Vol. 1, 2 (Kluwer Acad. Publ., Dordrecht, 2003), pp. 83–174.

[36] H.V. Grushevskaya and N.G. Krylova, ”Effects of Finsler geometry in the physics of surface phenomena: the case of monolayer systems” (in Russian), Hypercomplex Numbers in Geometry and Systems. 8(15), 128–146 (2011).

[37] V. Balan, H. Grushevskaya and N. Krylova, ”Finsler geometry approach to thermodynamics of first order phase transitions in monolayers”, Diff. Geom. - Dyn. Systems 17, 24–31 (2015).

[38] G. Lippman, ”Relations entre les phénomènes électriques et capillaires”, Ann. Chim. Phys. 5, 494–549 (1875).

[39] A. Frumkin, Couche Double. Electrocapillarite (Herman et Cie, Paris, 1936).

[40] L.D. Landau and E.M. Lifshitz, Electrodynamics of Continuous Media (Science, Moscow, 1982).

[41] J.W. Gibbs, The Collected Works of J. Willard Gibbs, Vol.1 (Longmans, Green & co., New York, 1931).
[42] M. Neagu, N.G. Krylova and H.V. Grushevskaya, "Jet theoretical Yang-Mills energy in the geometric dynamics of two dimensional monolayers", J. Math. Phys. 54, 031508 (14pp.) (2013).

[43] S. Kobayashi and K. Nomizu, Foundations of Differential Geometry, Vol. 1, Chap.2, 3 (Wiley-Interscience, 1996).

[44] R. Miron, D. Hrimiuc, H. Shimada and S.V. Sabau, The Geometry of Hamilton and Lagrange Spaces (Kluwer Academic Publishers, New York, Dordrecht, London, Moscow, 2001).

[45] V. Balan, H. Grushevskaya, N. Krylova, M. Neagu and A. Oana, "On the Berwald-Lagrange scalar curvature in the structuring process of the LB-monolayer", Applied Sciences 15, 30–42 (2013).