Finsler geometry approach to thermodynamics of first order phase transitions in monolayers

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Abstract. We present a geometrical approach to the thermodynamics of first order phase transitions in the compressed monolayer on the interphase boundary between air and water. The dependence of the compressibility curvature $\kappa$ on the Berwald curvature of the monolayer space has been described for a spherically symmetric monolayer in the metastable state. As well, the similarity of calculations compared to experimental data, sustains the idea that the Finsler anisotropic framework represents an appropriate environment for modeling the thermodynamics of compressed monolayers.


Key words: Finsler structure; Berwald curvature; flag curvature; first order phase transition.

1 Introduction

Phase transition of the first order is characterized by fluctuations of the thermodynamic parameters which are considered within a continuous critical region of the parameters, rather than at some critical point (like in the 2-nd order phase transition). At the compression of a Langmuir monomolecular layer (monolayer), the value of surface tension $\tilde{\tau}$ does not change in the phase transition region, although the area $S$ per one molecule changes. Due to this, one may observe a phase coexistence plateau in the $\tilde{\tau} - S$ isotherm. The known procedures (e.g., [9]) which handle the statistical analysis of experimental data of monolayer compressibility $\kappa$ in the whole region of surface pressure $\tilde{\tau}$ allow us to determine only the mean value of the compressibility coefficient – the "apparent" compressibility $C'$ in relatively linear sections of the isotherms. To reveal the behavior of the compressibility coefficient $\kappa$ on the critical surface of surface pressure values, the statistical procedure needs to be applied to huge experimental data arrays.

In the case of the 2-nd order phase transition, such statistical data analysis can be carried out by renormalization group methods. Up to this moment, there exists no generally recognized standard suitable statistical analysis of the $\tilde{\tau} - S$ compression isotherm. However, in [3, 1], a geometrical approach was proposed, which describes a
compressed monolayer structuring on the air/water interface. The compressibility $\kappa$ of a spherically symmetric monolayer was expressed by means of the Finslerian flag curvature.

The goal of the present study is to propose a Finsler geometry approach to the thermodynamics of first order phase transitions in two-dimensional systems, and to describe an abnormally large dispersion of the compressibility coefficient $\kappa$ in the critical region of isotherms of the compressed monolayer on the water surface. It is shown that the metastable states of the matter behave like instanton-like regions, and that the crystal structure formation is characterized by two-anomalous traces of the Berwald curvature. Also, a comparison of the dependence of $\kappa$ on the surface pressure $\tilde{\pi}$ with the experimental data is performed, revealing a scenario of phase transition in iron-containing monolayers of the thiophene-pyrrole series oligomer.

2 Lagrange–Berwald structures for amphiphilic membranes

The amphiphilic molecules of fat acids form a monolayer on the surface of the water subphase. Electrocapillarity phenomena take place on the phase interface. The magnitude of the surface tension $\sigma$ of such a 2-dimensional membrane is determined by the electrocapillary forces which act on the monolayer [5].

It may be observed that the first order phase transition occurs for a long compression time $\Delta t \gg 1$. The experimentally measured quantity, interpreted as the surface pressure of the monolayer $\tilde{\pi}$, is defined by the expression

$$\tilde{\pi} = \sigma_{H_2O} - \sigma_{\text{hydrocomp}}$$

where $\sigma_{H_2O}$ 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 (2.1), 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 consequence of the diminishing of the Langmuir monolayer density $\rho$ due to the complexes decay, the increment of surface pressure $\Delta \tilde{\pi}$ observed during the phase transition of $\Delta t$, 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 a parameter $\tau$ – as a parameter of the current state of the process of the first order phase transition – in hydrated complex monolayers only. Then, the derivative $\frac{\partial \tilde{\pi}}{\partial \tau}$ is the rate of change of the surface pressure of the hydrated complexes monolayer. Taking into consideration that $\frac{\partial (\tilde{\pi})}{\partial \tau} \propto -\frac{\partial (V_{\text{LH}})}{\partial \tau} \propto k_B T \frac{\partial \rho}{\partial \tau} \propto k_B T \tilde{C}$, and $\frac{\partial \tilde{C}}{\partial \tau} \propto C' V$, that $C'$, $\tilde{C}$ and the temperature $k_B T$ are constants, and that the change of the surface $S$ per one molecule is proportional to the square of variation $\delta r (\tau)^2$, we yield a space–time derivative of the compressibility coefficient $\kappa = \frac{1}{S} \frac{\partial S}{\partial \tau}$.

$$\frac{\partial \kappa}{\partial \tau} = -\frac{1}{S \Delta t_{\text{LH}}} \frac{\partial^2 S}{\partial \tilde{\pi} \partial \tau} = \frac{2}{k_B T C'' \delta \tau} \frac{\partial^2 (\delta r \tau)}{\partial \tau^2}$$
where $\kappa'_s = \frac{\partial^2}{\partial s^2} \propto \frac{\kappa}{\Delta t_{ph}}$, $C'' = C' \tilde{C}$, ($C' \tilde{C} > 0$), and where $\Delta t_{ph}$ is the compression time of the system in the state of phase transition.

The Lagrangian of the system under the above considerations can be represented as

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

where the electrocapillary potential energy $U(r, t)$ is given by

\[
U(r, t) = \frac{2}{3} \pi^2 q^2 \rho_0^2 \frac{1}{\varepsilon \varepsilon_0 R_0^2}.
\]

A method was proposed in [6], which describes and computes the dispersion of the pencil of the geodesics within the monolayer (given by Jacobi fields) in the neighborhood of the instanton-like solution of the system (2.3). In this context, Fig. 1 illustrates the behavior of the Jacobi fields for the system (2.3) in the metastable state, where the Jacobi field $\delta r(s) = \delta r_i(s) \tilde{N}$, ($|\tilde{N}| = 1$) was considered along the geodesic $x^i(s)$ with the normal $N$, and was defined by the flag curvature $K$ by means of $\frac{d^2 \delta r(s)}{ds^2} = -K \cdot \delta r$ ([2]).

According to Fig. 1, the dynamics of the particles in a monolayer does not change during the time of compression $\Delta t$, which does not exceed the value $\sim 0.005$. It can be noted that at the compression time $\Delta t > 0.007$, the system periodically loses (for $K < 0$) and restores (for $K > 0$) its stability, and that the unstable phases become stable and vice versa. Therefore, such phases may coexist, which makes the distinctive feature of first order phase transitions.

\[
\begin{align*}
\Delta t & = \frac{d}{ds} \cdot \Delta s_i = T_i, \quad i = 1, 2, 3, \ldots,
\end{align*}
\]

Fig. 1. The dependence of deviation $\delta r$ on the time interval $\Delta t$.

In this way, the system periodically loses and then recaptures stability for the different, but finite time intervals $\Delta t_i = \frac{d}{ds} \cdot \Delta s_i = T_i$, $i = 1, 2, 3, \ldots$, which are
shown in Fig. 1. The curvature $K$ in the first order phase transition turns out to be not a scalar, but a function dependent on the flag $\{\frac{dt}{dx_i}, \hat{N}(s_i)\}$, $i = 1, 2, 3, \ldots$.

In the formalism of Lagrange spaces, the presence of a discrete set of curvatures $K(t, \hat{r}; \{\frac{dt}{dx_i}, \hat{N}(s_i)\})$ provides a non-conclusive relationship between the curvature $K$ and the thermodynamic values (the compressibility of the monolayer $\kappa$).

With the help of the evolution parameter $\tau$, one may complete the discrete set of parameters $\Delta t_i, i = 1, 2, 3, \ldots$ up to the differential of a smooth function $dt = \xi d\tau$, $\dot{\xi} = \frac{dt}{d\tau}$, and obtain the parameterized three-dimensional space–time of the monolayer $M_F$ with coordinates $(r(\tau), \phi(\tau), t(\tau))$.

The specific feature of this approach is that instead of a discrete set $K(\Delta t_i, \hat{r})$, we have a parameterized the curvature $K(\tau, t, \hat{r}, \dot{\xi})$, based on which one can investigate the thermodynamics of the first order phase transitions. We further shall show that the metric fundamental function on $M_F$ is a pseudo-Finsler one.

3 The Finslerian background of the problem

We further consider the parameterized action of the problem (2.3) as

$$
(3.1) \quad dl_F = mc^2 \dot{\xi} d\tau - L(\tau) \dot{\xi} d\tau = \left(\frac{A \dot{\xi}^2}{\dot{r}} + B \dot{\xi} - C (\dot{r}^2 + \dot{\phi}^2) \right) d\tau,
$$

where the parameters $A$, $B$, and $C$ are given by

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

Here $\dot{\xi}$, $\dot{r}$, and $\dot{\phi}$ correspond to the derivatives of $t$, $r$, and $\varphi$ with respect to the evolution parameter $\tau$, respectively. The parametrized Lagrangian $L(\Delta \xi, \tau) = L(\tau) \dot{\xi}$ which enters (3.1), is a positive-homogeneous of first order function. It hence defines the arc-element for the space of linear elements, called also Finsler norm [8, 7]. Let $p_\xi$ be a generalized momentum conjugated to the velocity $\dot{\xi}$:

$$
(3.2) \quad p_\xi = \frac{\partial L(\Delta \xi, \tau)}{\partial \Delta \xi}.
$$

Since the metric function $L(\Delta \xi, \tau)$ from (3.1) is a homogeneous function of first order relative to velocities, we have

$$
(3.3) \quad \frac{\partial L(\Delta \xi, \tau)}{\partial \Delta \xi} \Delta \xi = p_\xi \Delta \xi = L(\Delta \xi, \tau).$$

Let us examine the supporting function $H(\xi; \hat{r}; p_\xi, p_x, p_y)$ for the indicatrix. We note that $H(\xi; \hat{r}; p_\xi, p_x, p_y)$ plays the role of Hamiltonian of the problem, and is
determined by \( p_\xi \) as

\[
(3.4) \quad \dot{\xi} = H(\xi, \bar{x}; p_\xi, p_x, p_y) \frac{\partial H(\xi, \bar{x}; p_\xi, p_x, p_y)}{\partial p_\xi}.
\]

By fixing the energy \( E \) of the system: \( H(\xi, \bar{x}; p_\xi, p_x, p_y) = E \), one can integrate the equation (3.4):

\[
(3.5) \quad \int \dot{\xi} \, dp_\xi = EH(\xi, \bar{x}; p_\xi, p_x, p_y).
\]

The pseudo-Euclidean norm is - in our case - the analog of the mass surface \( E^2 - (\dot{\gamma})^2 = 1 \) with \( \dot{\xi} \sim E \). One can consider (3.5) as the indicatrix equation in the cotangent space:

\[
(3.6) \quad p_\xi - H(\xi, \bar{x}; p_\xi, p_x, p_y) = 0.
\]

Now, taking into account (3.3), one can write the square of the metric function \( F^2(x^1, \Delta x^1) \) for the system, whose dynamics takes place over the mass surface,

\[
(3.7) \quad F^2(x^1, \Delta x^1) = L(\Delta \xi, \tau) p_\xi \Delta \xi.
\]

By substituting (3.6) into (3.7), taking into account the equality \( p_\xi = E \), and making the following renormalization: \( p, m \rightarrow p/E, m/E \), one gets a metric function which describes the dynamics of our system on the mass surface:

\[
(3.8) \quad F^2(x^1, \Delta x^1) = A \frac{\Delta \xi^3}{\Delta \tau^2} + B \Delta \xi^2 - C \frac{(\Delta x^1 + \dot{\gamma})^2 \Delta \phi^2}{2E}.
\]

In the space endowed with the square of the metric function \( F^2(x^1, \Delta x^1) \) (3.8), the indicatrix supporting function \( H(x, y) \) (the Hamiltonian) of a moving particle takes an arbitrary fixed value \( E = \dot{\xi} \). One can further determine the first \( KCC \)-invariant:

\[
\varepsilon^i = G^i - \frac{\partial G^i}{\partial y^j} y^j
\]

where

\[
G^i(y) = \frac{3}{2} g^{i j}(y) \left\{ \frac{\partial^2 F^2(x, y)}{\partial x^k \partial y^j} y^k - \frac{\partial F^2(x, y)}{\partial x^k} y^k \right\} = \frac{3}{2} g^{i j}(y) \left\{ 2 \frac{\partial g^{i j}}{\partial x^k} (y) - \frac{\partial g_{ik}}{\partial x^j} (y) \right\} y^k y^j,
\]

and \( x = (x^1, x^2, x^3) = (t, r, \varphi) \) and \( y = (y^1, y^2, y^3) = (\xi, \dot{r}, \dot{\varphi}) \). The spray components \( G^i \) provided by \( F^2 \) (3.8) have the explicit form:

\[
\begin{align*}
G^1 &= \frac{A}{\Delta \tau^2} \left[ \frac{1}{2} A_t \xi^2 + B_t \xi^2 + \frac{3}{2} C r \xi^2 \frac{\Delta \tau}{\Delta \xi} \right] - \frac{C}{\Delta \tau^2} \left[ 2 A_t \xi^2 + B_t \xi^2 + 3 A_r \xi^2 + 2 B_r \xi^3 \right], \\
G^2 &= \frac{3}{4} \frac{A}{\Delta \tau^2} \left[ - A_r \xi^2 + \frac{1}{2} B_t \xi^2 + C r \xi^2 \frac{\Delta \tau}{\Delta \xi} \right] - \frac{B}{\Delta \tau^2} \left[ A_t \xi^2 + 2 A_r \xi^3 + B_t \xi^2 - C r \xi^2 \right], \\
G^3 &= \frac{1}{2} \dot{r} \dot{\varphi},
\end{align*}
\]

where

\[
\Delta_2 = \frac{3A^2}{4} \left( \frac{\xi}{r} \right)^4 + AB \left( \frac{\xi}{r} \right)^3 - \frac{3AC \xi}{2} \frac{\xi}{r} - \frac{BC}{2},
\]

\[
A_t = \frac{\partial A}{\partial t}, A_r = \frac{\partial A}{\partial r}, B_t = \frac{\partial B}{\partial t}, B_r = \frac{\partial B}{\partial r}.
\]
Similarly, the spray components \(G^i\) for the function \((dl^2_F)^2\) obtained from the expression (3.1) are:

\[
G^1 = \frac{A^3}{4A} \left[ \frac{1}{2} A_r \xi^2_r + B_r \xi^2_r + \frac{1}{2} B_t \xi^2_t + \frac{3}{2} C r \xi^2_r \xi^2_t \right] - \frac{C}{8A} \left[ 2A_r \xi^2_r + B_t \xi^2 + 3A_r \xi^2 + 2B_r \xi^t \right],
\]

\[
G^2 = \frac{A^3}{4A} \left[ -\frac{1}{2} A_r \xi^2_r + \frac{1}{2} B_t \xi^2_t + C r \xi^2_r \right] - \frac{1}{8A} \left[ A_r \xi^2_r + 2A_t \xi^2_t + B_t \xi^2 - C r \xi^2 \right],
\]

\[
- \frac{C}{8A} \left[ 3 - r^2 \xi^2 \right] \left[ A_r \xi^2_r + 2A_t \xi^2_t + B_r \xi^2 + 2(B_t - A_r) \xi^2 + C r \xi^2 \xi^2 \left( 1 + r^2 \xi^2 \right) \right],
\]

\[
G^3 = \frac{1}{2r} \dot{\varphi} + \frac{A^3}{4A} \frac{\xi^2_r}{\xi^2} \left[ A_r \xi^2_r + 2B_t \xi^2 + B_r + 3C r \xi^2 \right] - \frac{C}{8A} \varphi \xi^2 \left[ 2A_r \xi^2_r + (B_t + 3A_r) \xi^2 + 2B_r \right],
\]

where

\[
\Delta = \frac{1}{8} \left( 2A_r \xi^2 - C \right) \left( 2A_r \xi^2 + 2B - C \left( \frac{r^2}{\xi^2} + \varphi^2 \xi^2 \right) \right).
\]

The space \(M_F\) is pseudo-Finsler due to the fact that the first KCC-invariant for the metrics given by (3.1 and 3.8), identically vanishes:

\[
\varepsilon^i_{(dl^2_F)} = \varepsilon^i_F = 0.
\]

Let the time \(t(\tau)\) run at a unit constant rate, \(\dot{\xi} = 1\). This projective condition imposed on vector fields gives us a 2-dimensional Berwald–Lagrange space \(M_{BL}\) with non-trivial first KCC-invariant \(\varepsilon^i_{BL}, i = 1, 2:\)

\[
\varepsilon^1_{BL} = \frac{-p r^3 |V|(\dot{r})^3 e^{2|V|/r} \cdot \varphi - m(\dot{r})^6 \frac{\partial U(t, \tau)}{\partial r} - 2 p^2 r^9 |V|^3 \dot{r} e^{4|V|}}{(m(\dot{r})^3 - 2 p r^5 |V| e^{2|V|})^2},
\]

\[
\varepsilon^2_{BL} = 0,
\]

where

\[
\Theta = r^2 \frac{\partial U(t, \tau)}{\partial r} + m |V| \dot{r} (6 \dot{r} - 4 r) + 3 m r \left( \dot{\varphi}^2 \dot{\xi}^2 - 5 (\dot{r})^2 \right).
\]

### 4 The set of inflection points

We shall further examine the set of quasi-stationary states, at which \(\dot{r} = 0\), for all possible \(\dot{\varphi}\). In the 2-dimensional Berwald–Lagrange space \(M_{BL}\), according to (3.10), the first KCC-invariant vanishes along this set: \(\varepsilon^i_{BL} = 0, i = 1, 2\). The set of inflection points corresponds to singular instanton-like paths:

\[
\left( m(\dot{r})^3 - 2 p r^5 |V| e^{2|V|/r} \right)^2 = 0.
\]

In the 2-dimensional Berwald–Lagrange space, the first KCC-invariant (3.10) nontrivially diverges on this inflection set. Due to this feature, the set of inflection points is not visible within the Lagrangian formalism. In the case of the parametrized Lagrangian (3.1), the first KCC-invariant \(\varepsilon^2_F\) is defined on both sets, and describes the transitions between the quasi-stationary states. Since the first KCC-invariant (3.9) identically vanishes, we conclude that the 3-dimensional parametrization of the Berwald–Lagrange space of the 2-dimensional monolayer naturally provides a pseudo-Finsler structure.
5 Anomalous dispersion of compressibility at large times of monolayer compression

Now, we can express the space–time derivative of the compressibility coefficient $\kappa$ from (2.2) by means of the scalar Berwald curvature $B_c = g^{ij} B_{ijkl} = g^{ij} \frac{\partial^2 \kappa}{\partial y^i \partial y^j}$ (the double trace of the Berwald curvature $B_{ijkl}^2$).

Since $\frac{\partial^2 \delta \tau}{\partial \tau^2} = -B_c \delta \tau$, after integration (2.2), and taking into account that $\frac{\partial^2 \tau}{\partial \tau} = \frac{\partial^2 \tau}{\partial \tau} \sim \Delta t_{phl}$, one gets the compressibility:

$$
\kappa = \kappa' \Delta t_{phl} \sim - \frac{1}{S} \int_{r(\varpi)}^{r(\varpi+\Delta t_{phl})} B_c d^2 r.
$$

The Berwald curvature $B_c$ is equal to zero everywhere except of the isotherm plateau. Therefore the expression (5.1) can be written as

$$
\kappa \sim - \frac{1}{S} \int_{r(0)}^{r(\Delta t_{phl})} B_c d^2 r = - \int_{r(0)}^{r(\Delta t_{phl})} \frac{\partial B_c}{\partial \tau} d^2 r = -(B_c(r(\Delta t_{phl})) - B_c(0)),
$$

where $B_c(0) \equiv B_c(r(0))$ is a constant of the phase transition. In Fig. 2, the experimental dependence of compressibility $\kappa$ on surface pressure $\bar{\pi}$ for the Fe-containing monolayer of thiophene-pyrrole oligomers [4] is described. This has been approximated by the illustrated calculation of $B_c$. The following parameters have been used:

- $B_c(0) = 0.04$, $\xi \equiv \Delta t_{phl} = 0.007$, $\dot{\gamma} = 3800$, $\xi = 20$, $\dot{\varphi} = \pi$, $V = 15$, $R_0 = 0.36$,
- the dielectric water permittivity is $\varepsilon = 81$, $\mu_0 q = 0.29$, and $m = 47 \cdot 10^{-26}$.

![Fig. 2. Experimental dependence of compressibility $\kappa$ on the surface pressure $\bar{\pi}$ for the iron-containing monolayer of thiophene-pyrrole oligomers (blue curve) and its theoretical approximation (red curve) for the isotherm constant level.](image)
6 Conclusions

The comparison of the dependence of $\kappa$ upon the surface pressure $\tilde{\pi}$ with experimental data has allowed to reveal a scenario of phase transition in the Fe-containing monolayers of thiophene-pyrrole series oligomers. The compressibility coefficient $\kappa$ has an abnormally large dispersion in the critical region on isotherm of the monolayer compressed on a water subphase surface. The metastable state of the matter appears as an instanton-like behaving region. The crystal structure formation is characterized by twice-anomalous trace of the Berwald curvature.

References


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