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GEOMETRICAL APPROACH TO PHASE TRANSITIONS AND SINGULARITIES OF LAGRANGIAN SUBMANIFOLDS

Introduction

The so-called critical state is observed for many substances. If, for example, ether is conducted to the point with the temperature 467 K, the preassure 35,5 atm. and the density 0.26 g/cm^3 then it exhibits unusual properties, which do not appear for other values of thermodynamical parameters. In this state appears the phenomenon of critical opalescence. The response functions, e.g. specific heats, isotermal compressibility, take great values. A neighbourhood of this point where such phenomena occurs is called a critical region (for the definitions see [8]).

On the basis of ideas proposed in [4] or [10] we try to adopt the geometric formulation of phenomenological thermodynamics (cf. [7]) to description of critical phenomena. In our approach the critical region is described by the stable singularities of lagrangian submanifolds (cf. [1]).

The main points of our approach are as follows:

1°. The principal objects are defined: the phase as a symplectic manifold with local chart (extensive and intensive parameters) in the neighbourhood of critical point, the space of equilibrium states of the concrete system as a lagrangian submanifold of phase space (Hypothesis I).

2°. The notion of stability of lagrangian submanifold is introduced and stability of space of equilibrium states is demanded (Hypothesis II). The stability property allows us to restrict arbitrariness in the choice of a realistic model of critical phenomena.

3^o. As a consequences of the hypotheses we obtain a local properties of the phase diagram (after a suitable modification e.g. Maxwell construction). Using the Legendre transformation and applying the classification theorem classifying the stable spaces of states (Theorem 4.3) we obtain, for a simple system, the critical exponents γ', β, δ (Theorem 5.1). The identical exponents were derived in the classical theories (Van der Waals theory, Landau's theory [8]). One of the consequences of our model is, obtained explicitely in the generic case, the low of "rectlinear diameter" (Corollary 5.2, on experimental verification of this law see [8]). The universality of critical exponents is a simple consequence of the applied methods, specially the stability notion.

2. Thermodynamic space

Let $X_1,\dots,X_{n+1}$ ($X_i > 0$ for $i = 1,2,\dots,n+1$) denote the set of extensive thermodynamic parameters (cf. [2]). U is the internal energy of the system. E - a function: $E: \mathbb{R}^{n+1} \to \mathbb{R}$. The function E provides the so-called fundamental equation: $U = E(X_1,\dots,X_{n+1})$. The first-order homogeneouity of the function E allows us to write this equation in the form $u := U/X_{n+1} = e(x_1,\dots,x_n) := E(x_1,\dots,x_n,1)$, where $x_i := X_i/X_{n+1}$ (thermodynamic densities). The first law of thermodynamics (infinitesimally) has the form $du = \sum_{i=1}^{n} p_i dx_i$, where p_i are the thermodynamic forces, which for a equilibrium state of the system are given by the following equations: $p_i := \partial e/\partial x_i$, $i = 1,2,\dots,n$, the so-called equations of state.

Let $(p_1^c,\dots,p_n^c,x_1^c,\dots,x_n^c)$ be coordinates of critical point (e.g. p_c, T_c, v_c, S_c for a simple system). We use the local coordinates $\{p_1',\dots,p_n',x_1',\dots,x_n'\} = \{p_1-p_1^c,\dots p_n-p_n^c, x_1-x_1^c,\dots,x_n-x_n^c\}$ and functions: $u' = e'(x_1',\dots,x_n') := e(x_1'+x_1^c,\dots,x_n'+x_n^c) - \sum_{i=1}^{n} p_i^c x_i'$, $du' = \sum_{i=1}^{n} p_i' dx_i'$.

Our considerations are rather local in a small neighbourhood of the critical point. Then throughout this paper we are confined to the germs at critical point of smooth objects i.e. germs of manifolds, functions, forms etc. To avoid unessential formal complications we use functions rather then germs (cf. [12]). This local approach lead to the following

H y p o t h e s i s I. A. The thermodynamic phase space of the system in the critical state is (isomorphic to) $\mathbb{R}^{2n}$ endowed with the canonical symplectic structure defined by 2-form $\omega = d\vartheta$, where ϑ is a 1-form of internal energy. In our case $\vartheta = \sum_{i=1}^{n} p_i' dx_i'$, where $\{p_1', \dots, p_n', x_1', \dots, x_n'\}$ are coordinates on $\mathbb{R}^{2n}$, as before.

B. The set of equilibrium states of concrete system is represented in $(\mathbb{R}^{2n}, \vartheta)$ by the lagrangian submanifold L (definitions see [10]), for which there exists a generating function e', called the internal energy, such that $L =$ $=$ graph de'.

Further on we will write x_i, p_i, e, u instead of x_i', p_i', e', u', and $\mathbb{R}^{2n} = \mathbb{R}^n \times \mathbb{R}^n = P \times X$, where $P \overset{df}{=} \mathbb{R}^n$ with the local coordinates $\{p_1, \dots, p_n\}$, $X \overset{df}{=} \mathbb{R}^n$ with the local coordinates $\{x_1, \dots, x_n\}$. We have the canonical fibre structures $\pi_1 : \mathbb{R}^{2n} \to P$, $\pi_2 : \mathbb{R}^{2n} \to X$.

R e m a r k 2.1. Consider the simple system. According to Hypothesis I, $(x_1, x_2) \to e(x_1, x_2)$ is the fundamental equation, x_1 - entropy (of one mole), x_2 - volume. From the experimental data (cf. [8]) it follows that the function e has a degenerated critical point at zero. It is observed that the specific heats C_p, C_v and isothermal compressibility K_T (the response functions) tends to infinity if the state of system is nearer and nearer to the critical point i.e. $C_p, C_v, K_T \to \infty$ if $T \to T_c$. This divergence is connected with the degree of degeneracy of singularity of function e. An example of the simple system where the phase transitions not appear is a ideal gas. In this case e and g are the regular functions.

3. Stability of the space of equilibrium states

Let (M,P,π) be a differential fibration and ϑ a 1-form on the manifold M. The quadruple (M,P,π,ϑ) is called a special symplectic structure on M if there is a diffeomorphism $\alpha: M \to T^*P$ such that $\pi = \pi_P \circ \alpha$, $\vartheta = \alpha^* \vartheta_P$, where $\pi_P: T^*P \to P$ and ϑ_P is the canonical symplectic 1-form on T^*P (see [10]).

On the phase space we have two special symplectic structures $(\mathbb{R}^{2n}, P, \pi_1, \vartheta_1 = -\sum_{i=1}^{n} x_i dp_i)$ and $(\mathbb{R}^{2n}, X, \pi_2, \vartheta_2 = \sum_{i=1}^{n} p_i dx_i)$. (The two so-called control modes, see [4]). Let $(L_1,0)$, $(L_2,0)$ be the two germs at zero of the lagrangian submanifolds in $(\mathbb{R}^{2n}, P, \pi_1, \vartheta_1)$. We say that $(L_1,0)$ and $(L_2,0)$ are equivalent if and only if there exists a symplectomorphism (germ) Φ of the fibre space $(\mathbb{R}^{2n}, P, \pi_1)$, $\Phi: (\mathbb{R}^{2n},0) \to (\mathbb{R}^{2n},0)$ and diffeomorphism $\psi: (P,0) \to (P,0)$ such that $\pi_1 \circ \Phi = \psi \circ \pi_1$, $\Phi(L_1) = L_2$. Let $(L_1,0)$, $(L_2,0)$ are given by the embeddings $i_1, i_2: (\mathbb{R}^n,0) \to (\mathbb{R}^{2n},0)$, so we have the two mappings, the so-called lagrangian mappings: $\pi_1 \circ i_1$, $\pi_2 \circ i_2: \mathbb{R}^n \to P$.

R e m a r k 3.1. If L_1, L_2 are equivalent then the respective lagrangian mappings are equivalent in the sense of the theory of stable smooth mappings (cf. [3]).

Let us consider the space of embeddings of lagrangian submanifolds endowed with the Whitney C^∞-topology (cf. [11]). We state that the two lagrangian submanifolds are neighbouring if the respective embeddings are neighbouring.

D e f i n i t i o n 3.2. The lagrangian submanifold $L_1 \subset \mathbb{R}^{2n}$ is called stable if there exists an open neighbourhood of the embedding $i_1: \mathbb{R}^n \to \mathbb{R}^{2n}$, of this submanifold, such that every submanifold from this neighbourhood is equivalent to L_1.

Locally: We say that the germ $(L_1,0)$ is stable if for every open neighbourhood U of the origin in $\mathbb{R}^{2n}$ there exist an open neighbourhood of the submanifold L_1 such that for every point L of this neighbourhood there exists $p \in U$ that $(L_1,0)$ and (L,p) are equivalent (see [11]).

The next step of our construction is the following

H y p o t h e s i s II. The space of equilibrium states of the thermodynamical system is a stable lagrangian submanifold in the phase space with the special symplectic structure $(\mathbb{R}^{2n},P,\pi_1,\vartheta_1)$.

Now the problem of local structure of the phase diagram in the critical region can be taken up (cf. [2]). Let L be the space of states of the system and i the embedding of this space into the phase space. We denote $\tau := \pi_1 \circ i$ and $CL := \{x \in \mathbb{R}^n: \dim \operatorname{Ker} \tau^*(x) \neq 0\}$. The sets $I := \tau(CL) \subset P$ and $i(CL)$ are called the limiting phase diagram (appear contour) and respectively the limiting set of metastable states (spinodal curve). The set I provides us the phase diagram (as in thermodynamics) after some convencional modifications.

4. Local properties of the stable phase diagrams

On the basis of Hypothesis I the space of states L is generated by the internal energy e (with respect to the structure $(\mathbb{R}^{2n},X,\pi_2,\vartheta_2)$).

R e m a r k 4.1. An assumption of the Hypothesis I.B. is a generic property, i.e. the case of lagrangian submanifold for which there exist a generating function e is typical as in the following proposition.

P r o p o s i t i o n 4.2. The subset in the space of germs of lagrangian submanifolds such that for every submanifold $(L,0)$, from this subset, there exists a germ of smooth function $e: (X,0) \longrightarrow \mathbb{R}$ generating the submanifold $(L,0)$ is open and dense. An every submanifold $(L,0)$ is equivalent to such which in the special structure $(\mathbb{R}^{2n},X,\pi_2,\vartheta_2)$, has a generating function.

P r o o f . See for example [1].

Let us denote $KL := \{x \in X: \det(\partial^2 e/\partial x_i \partial x_j)(x) = 0\}$ and $de : X \longrightarrow T^*X = \mathbb{R}^{2n}$. It is easy to verify that for the spinodal curve we have $i(CL) = de(KL)$.

Let g be a generating function (Gibbs energy) of L in the special structure $(\mathbb{R}^{2n}, P, \pi_1, \vartheta_1)$. The transition from the representation of lagrangian submanifold L by generating function with respect to $(\mathbb{R}^{2n}, P, \pi_1, \vartheta_1)$, to the representation by generating function with respect to $(\mathbb{R}^{2n}, X, \pi_2, \vartheta_2)$ is called the Legendre transformation (cf. [10]).

For further considerations we assume that $0 \in KL$ is a degenerated and isolated critical point of function e, besides we assume that e has a finitely determined singularity. This means that the ideal, in the ring of germs at zero of smooth functions, generated by $\partial e/\partial x_1, \ldots, \partial e/\partial x_n$ includes a power of the maximal ideal. Because e is a finitely determined germ, KL is an algebraic set (cf. [3]). In the same way the set I is also algebraic (locally), so there exists a finite stratification of I, namely $I = I^1_1 \cup \ldots \cup I^1_{k_1} \cup I^2_1 \cup \ldots \cup I^2_{k_2} \cup \ldots \cup I^n_{k_n}$, where $I^i_{k_i}$ is a stratum of codimension i.

Let $\mathcal{O}$ be a small open neighbourhood of zero in P. The set $\mathcal{O} - I = \sum_{i=1}^{m} \mathcal{O}_i$ decomposes into open connected parts. The piece of lagrangian submanifold L_{ji} over $\mathcal{O}_i$ has a generating function g_{ji}. The transition by the Legendre transformation to the structure $(\mathbb{R}^{2n}, X, \pi_2, \vartheta_2)$, transforms the functions g_{ji} onto $e|_{\pi_2(L_{ji})}$, so that $g_{ij}(p_1, \ldots, p_n) = e(x_1, \ldots, x_n) - \sum_{i=1}^{n} p_i x_i$, where x depends on p as follows: $p_i = \partial e/\partial x_i(x)$, $i = 1, \ldots, n$, $p \in \mathcal{O}_i$.

T h e o r e m 4.3. For the stable space of equilibrium states L, $\dim L < 6$, the Gibbs potential g_{ji} has the form

$$g_{ji} = F_{ji} \circ \theta + \Psi,$$

where: Θ -diffeomorphism, $\Theta:(P,0)\longrightarrow(P,0)$, Ψ - smooth function on P. F_{ji} is a Legendre transformation of the function $f\big|_{\pi_2(K_{ji})}$, where the function f generating lagrangian submanifold K with respect to the structure $(\mathbb{R}^{2n},X,\pi_2,\vartheta_2)$ is one from the following list:

dim L = 1. $A_1: f = x_1^2$, $A_2: f = \pm x_1^3$.

dim L = 2. $A_1: f = x_1^2+x_2^2$, $A_2: f = \pm x_1^3+x_2^2$, $A_3: f = \pm x_1^4+(x_2+x_1^2)^2$.

dim L = 3. $A_1: f = x_1^2+x_2^2+x_3^2$, $A_2: f = \pm x_1^3+x_2^2+x_3^2$, $A_3: f = \pm x_1^4+x_3^2+(x_2+x_1^2)^2$, $A_4: f = \pm x_1^5+(x_3+x_1^3)^2+(x_2+x_1^2)^2$,

$D_4: f = \pm x_1^2x_2\pm x_2^3+(x_3+x_2^2)^2$.

dim L = 4. $A_1: f = x_1^2+x_2^2+x_3^2+x_4^2$, $A_2: f = \pm x_1^3+x_2^2+x_3^2+x_5^2$,

$A_3: f = \pm x_1^4+(x_2+x_1^2)^2+x_3^2+x_4^2$, $A_4: f = \pm x_1^5+(x_3+x_1^3)^2+(x_2+x_1^2)^2+x_4^2$, $A_5: f = \pm x_1^6+(x_4+x_1^4)^2+(x_3+x_1^3)^2+(x_2+x_1^2)^2$,

$D_4: f = \pm x_1^2x_2\pm x_2^3+(x_3+x_2^2)^2+x_4^2$, $D_5: f = \pm x_1^2x_2\pm x_2^4+(x_4+x_2^3)^2+(x_3+x_2^2)^2$.

dim L = 5. $A_1: f = x_1^2+x_2^2+x_3^2+x_4^2+x_5^2$, $A_2: f = \pm x_1^3+x_2^2+x_3^2+x_4^2+x_5^2$,

$A_3: f = \pm x_1^4+(x_2+x_1^2)^2+x_3^2+x_4^2+x_5^2$, $A_4: f = \pm x_1^5+(x_3+x_1^3)^2+(x_2+x_1^2)^2+x_4^2+x_5^2$, $A_5: f = \pm x_1^6+(x_4+x_1^4)^2+(x_2+x_1^2)^2+x_5^2$,

$A_6: f = \pm x_1^2x_2\pm x_2^3+(x_3+x_2^2)^2+x_4^2+x_5^2$, $D_5: f = \pm x_1^2x_2\pm x_2^4+(x_4+x_2^3)^2+(x_3+x_2^2)^2+x_5^2$, $D_6: f = \pm x_1^2x_2\pm x_2^5+(x_5+x_2^4)^2+(x_4+x_2^3)^2+(x_3+x_2^2)^2$, $E_6: f = \pm x_1^3\pm x_2^4+(x_5+x_1x_2^2)^2+(x_4+x_1x_2)^2+(x_3+x_2^2)^2$.

P r o o f . Let $(L,0)$ be a germ of lagrangian submanifold, $L \subset T^*\mathbb{R}^n$ and Φ symplectomorphism of the fiber space $T^*\mathbb{R}^n \cong \mathbb{R}^{2n}$, $\Phi: (T^*\mathbb{R}^n,0) \longrightarrow (T^*\mathbb{R}^n,0)$. We need the following lemma (see e.g. [11]).

L e m m a . Let Φ be a lagrangian equivalence of $T^*\mathbb{R}^n$. Then

a) Φ is uniquely determined by a pair (Θ, ψ), where Θ-diffeomorphism $\Theta: (\mathbb{R}^n,0) \longrightarrow (\mathbb{R}^n,0)$, ψ-smooth function (up to additive constant) and $\Theta \circ \pi = \pi \circ \Phi$ ($\pi: T^*\mathbb{R}^n \longrightarrow \mathbb{R}^n$-projection).

b) If F_L is a generating function of $(L,0)$ then the generating function of $F_{\Phi(L)}$ has the form

$$F_{\Phi(L)} = F_L \circ \Theta^{-1} + \psi.$$

P r o o f . Using local coordinates we have, $\Phi:(p,q) := (p_1,\dots,p_n, q^1,\dots,q^n) \longrightarrow (P,\Theta) = (P_1(p,q),\dots,P_n(p,q), Q^1(q),\dots,Q^n(q))$ and $[q^i,q^j] = 0$, $[q^i,p_j] = \delta^i_j$, $[p_i,p_j] = 0$, $1 \leqslant i,j \leqslant n$, where $[u^i,u^j]$ are the Lagrange bracets (cf. [10]), $[u^i,u^j] := \sum_{k=1}^{n} \left(\frac{\partial Q^k}{\partial u^i}\frac{\partial P_k}{\partial u^j} - \frac{\partial Q^k}{\partial u^j}\frac{\partial P_k}{\partial u^i}\right)$. Hence we obtain two conditions

$$\sum_{k=1}^{n} \frac{\partial P_k}{\partial p_j}\frac{\partial Q^k}{\partial q^i} = \delta^j_i, \qquad \sum_{k=1}^{n} \frac{\partial P_k}{\partial q^j}\frac{\partial Q^k}{\partial q^i} = \sum_{k=1}^{n} \frac{\partial P_k}{\partial q^i}\frac{\partial Q^k}{\partial q^j},$$

in the matrix form

$$\text{(i)} \qquad (D_pP)(D_q\Theta)^T = I, \quad (D_qP)(D_q\Theta)^T = ((D_qP)(D_q\Theta)^T)^T,$$

where $D_pP := (\partial P_i/\partial p_j)_{1 \leqslant i,j \leqslant n}$.

Integrating the first equation of (i) we obtain

$$\text{(ii)} \qquad P(D_q\Theta)^T = p + \varphi(q),$$

where $\varphi:(\mathbb{R}^n,0) \longrightarrow \mathbb{R}^n$ is a smooth mapping.

Now we prove that $\partial\varphi_j/\partial q^i = \partial\varphi_i/\partial q^j$ $(1 \leqslant i,j \leqslant n)$, namely: Differentiating of (ii) we get an equation, $(D_q P)(D_q\Theta)^T + PD_q(D_q\Theta)^T = D_q\varphi$. Symmetricity of the first term of this equation is obvious on the basis of (i) and the second term is symmetric on the basis of equality $\sum_{k=1}^{n} P_k\ \partial^2 Q^k/\partial q^i \partial q^j = \sum_{k=1}^{n} P_k\ \partial^2 Q^k/\partial q^j \partial q^i$. Hence there exist a function $\bar{\psi}:(\mathbb{R}^n,0) \longrightarrow \mathbb{R}$ such that $\varphi = \left(\frac{\partial\bar{\psi}}{\partial q_1}, \dots, \frac{\partial\bar{\psi}}{\partial q_n}\right)$. This completes the proof of part a) of our Lemma, i.e.

$$\text{(iii)} \qquad P = (p + D_q\bar{\psi})((D_q\Theta)^T)^{-1}.$$

Let $F_{\Phi(L)}$ be a generating function of $\Phi(L)$. Then $(D_Q F_{\Phi(L)})(Q) = P(Q)$, and by (iii) we have

$$\text{(iv)} \qquad (p + D_q\bar{\psi})((D_q\Theta)^T)^{-1} = (D_Q F_{\Phi(L)}) \circ \Theta,$$

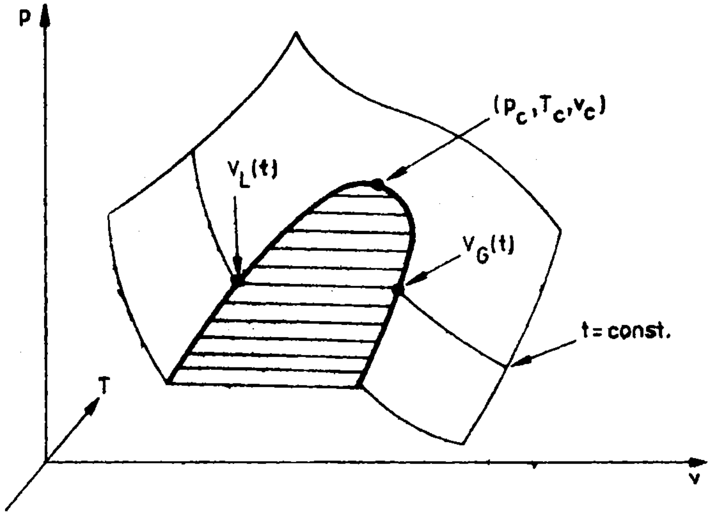
but $p = D_q F_L$. Substituting this into (iv) we get: $D_q(F_L + \bar{\psi}) = D_q(F_{\Phi(L)} \circ \Theta)$. At the end $F_{\Phi(L)} = F_L \circ \Theta^{-1} + \psi$, where $\psi = \bar{\psi} \circ \Theta^{-1}$, which completes the proof of our Lemma.

In the open neighbourhood of every point of a stable lagrangian submanifold L, $\dim L < 6$, we can take a symplectomorphism $\Phi = (\Theta,\psi)$ such that the generating function of submanifold $K := \Phi(L)$, with respect to the structure $(\mathbb{R}^{2n}, X, \pi_2, \vartheta_2)$, is one from the above mentioned list (see Theorem 11.3 in [1]). If we return to the special symplectic structure $(\mathbb{R}^{2n}, F, \pi_1, \vartheta_1)$, then by the Lagrange transformation we obtain the generating functions of the respective pieces of submanifold K. By the Lemma, which has been proved above, we have the generating function of the piece of $L = \Phi^{-1}(K)$ what was required in the thesis of Theorem 4.3.

5. Generic critical exponents for the simple system

Let us denote by $t = T_c - T$, $p = \bar{p} - p_c$ the intensive parameters, where T_c, p_c are the coordinates of critical point, T and $\bar{p}$ the temperature and the preassure. Let (s,ϑ) be an extensive variables at a neighbourhood of (s_c,v_c), where $v = \vartheta + v_c$ is the volume of one mole of the system, s - entropy, (s_c,v_c) - coordinates of a critical point (cf. [8]), $g:(t,p) \to g(t,p)$ - Gibbs potential. The second derivatives of g, at the critical region, provides us an important information about the thermodynamical properties of the system. An exponents in the infinitesimal power-laws of divergences of these derivatives are called the critical exponents.

Let us take a real isothermal process conducted under temperature t. We denote by $v_G(t)$, $v_L(t)$ the molar volumes of gas and liquid phases, respectively, at the limiting points of the set of coexistance phases (as in Figure below)



Now we can introduce the respective critical exponents (cf. [8]):

β : $(v_G - v_L)(t) \sim (t)^{\beta}$, $t > 0$,

γ' : $K_T\Big|_{v_L(t)} \sim (t)^{-\gamma'}$, $t > 0$,

K_T - isothermal compressibility, $K_T := -\frac{1}{V}\frac{\partial^2 g}{\partial p^2}$

δ : $p(\vartheta) \sim (\operatorname{sgn}\vartheta)|\vartheta|^{\delta}$, $t = 0$.

In the case of our simple system dim L = 2. According to Theorem 4.3 as stable there can appear the following lagrangian submanifolds: A_1, A_2, A_3. Hence we can say that in the neighbourhood of a fixed equilibrium state, the space of states has one of the mentioned above singularities. The more detailed treatment is as follows.

A_1) In the neighbourhood of such point the space L has a "good" projection both on X and P. The Gibbs potential g is a regular function, thus such point is not identified with the critical point, and is called a regular point of L.

A_2) Such states corresponds to a totally unstable states (thermodynamic stability [2]), in the neighbourhood of which there are the regular metastable states.

A_3) In the stable case such points appears as an isolated points adhering to the set of codimension one of A_2 -points and to the set of codimension zero of A_1 -points. The A_3 - points we identify with the critical points of matter.

Let $P \times X$, with the coordinates $\{t,p,s,v\}$, be a phase space of the system. By G we denote the group of preserving zero symplectomorphisms of the special structure $(P\times X, P, \pi_1, \vartheta_1)$. Let $L \subset P\times X \cong \mathbb{R}^4$ be a space of equilibrium states possessing at zero the singular point of type A_3. As a conclusion of this assumption we obtains the following

T h e o r e m 5.1. There exists an open and dense subset of the space of germs of lagrangian submanifolds of type A_3 such that for every element of this set we have the following values of critical exponents

$$\beta = 1/2, \quad \gamma' = 1, \quad \delta = 3.$$

(the critical exponents are the invariants of action of deformation group G in this subset).

P r o o f . By Theorem 4.3 we take the function $f(x_1,x_2) = \pm x_1^4 + (x_2+x_1^2)^2$. The Legendre transformation of a piece K_{ij} of lagrangian submanifold K has a form:

(i) $$F_{ij}(y_1,y_2) = \pm x_1^4+(x_2+x_1^2)^2-x_1y_1-x_2y_2$$

(ii) $$y = \pm 4x_1^3+4x_1(x_2+x_1^2), \quad y_2 = 2(x_2+x_1^2).$$

Hence the Gibbs potential $g_{ij}(t,p) = (F_{ij}\circ\Theta)(t,p) + \psi(t,p), (t,p) \in \mathcal{O}_j$, where $\Theta:(t,p) \longrightarrow (Y_1(t,p), Y_2(t,p))$-diffeomorphism $\Theta(0) = 0$, ψ- smooth function. In this case for $j = 1$ we have $i = 1$ and for $j = 2$, $i = 1,2,3$. For the present we omit the indices i,j. The volume has the form: $\vartheta(t,p) := (\partial g/\partial p)(t,p)$ and the set CK is given by the equation

(iii) $$x_2+(1\pm 3)x_1^2 = 0.$$

Taking x_2 from (ii) and substituting it to (i) we obtains: $g(t,p) = -\frac{3}{4}x_1Y_1(t,p) + \frac{1}{2}x_1^2Y_2(t,p) - \frac{1}{4}Y_2^2(t,p) + \psi(t,p)$, $Y_1(t,p) = \pm 4x_1^3+2x_1Y_2(t,p)$, where x_1 is a parameter.

If $(t,p) \longrightarrow X_1(t,p)$ is a solution of the equation

(iv) $$0 = R(\cdot,\cdot,X_1(\cdot,\cdot)), \quad R(t,p,x_1) = \pm 4x_1^3+2x_1Y_2(t,p)-Y_1(t,p),$$

then it is easy to see that

(v) $$\vartheta = -X_1\frac{\partial Y_1}{\partial p} + X_1^2\frac{\partial Y_2}{\partial p} - \frac{1}{2}Y_2\frac{\partial Y_2}{\partial p} + \frac{\partial \psi}{\partial p}.$$

Let $s \longrightarrow (\bar{t}(s),\bar{p}(s))$ be a smooth parametrization of the curve (iii) such that

(vi) $$Y_1(\bar{t}(s),\bar{p}(s)) \pm 8s^3 \overset{s}{\equiv} 0, \quad Y_2(\bar{t}(s),\bar{p}(s)) \pm 6s^2 \overset{s}{\equiv} 0.$$

The above system satisfies the assumptions of Implicit Function Theorem. Let $Y_1(t,p) = \alpha_1 t + \alpha_2 p \pmod{\mathfrak{M}^2}$, $Y_2(t,p) = \beta_1 t + \beta_2 p \pmod{\mathfrak{M}^2}$ ($\mathfrak{M}$ is a maximal ideal of the ring of germs of smooth functions). It follows from (vi) that $\bar{t}(s) = A_\pm s^2 + O(s^3)$, $\bar{p}(s) = B_\pm s^2 + O(s^3)$, where $A_\pm = \pm 6\alpha_2/(\alpha_1\beta_2 - \beta_1\alpha_2)$, $B_\pm = \pm 6\alpha_1/(\alpha_1\beta_2 - \beta_1\alpha_2)$. Following the generic assumption $\alpha_2 \neq 0$, $\alpha_1 \neq 0$ there exist the smooth functions φ_1, φ_2 such that $\bar{t}(s) = \mathrm{sgn}(A_\pm)\varphi_1^2(s)$, $\bar{p}(s) = \mathrm{sgn}(B_\pm)\varphi_2^2(s)$ and $(d\varphi_1/ds)(0) \neq 0 \neq (d\varphi_2/ds)(0)$. Hence the phase diagram has a general form: $p = \mathrm{sgn}(B_\pm)\varphi_2 \circ \varphi_1^{-1} \cdot (\varepsilon(\mathrm{sgn}(A_\pm)t)^{1/2})$, $\varepsilon = \pm 1$, and also

(vii) $$p(t) = (B_\pm/A_\pm)t + O_\varepsilon(((\mathrm{sgn}(A_\pm)t)^{1/2})^3),$$

where $B_\pm/A_\pm$ is a slope of coexistence curve (Clapeyron law).

Substituting (vii) to (v) we can define

(viii) $$v^\varepsilon(t) = v_c + (\varepsilon/\sqrt{|A_\pm|})(t\,\mathrm{sgn}(A_\pm))^{1/2} + O_\varepsilon(((t\,\mathrm{sgn}(A_\pm))^{1/2})^2)$$

and $v_G(t) := v^{+1}(t)$, $v_L(t) := v^{-1}(t)$.

As a conclusion we obtain $\beta = 1/2$.

Differentiating (iv) and (v) with respect to p we get the function

(ix) $$\frac{\partial v}{\partial p} = -\frac{\partial X_1}{\partial p}\frac{\partial Y_1}{\partial p} - X_1\frac{\partial^2 Y_1}{\partial p^2} + 2\frac{\partial X_1}{\partial p}X_1\frac{\partial Y_2}{\partial p} + X_1^2\frac{\partial^2 Y_2}{\partial p^2} - \frac{1}{2}\frac{\partial Y_2^2}{\partial p} - \frac{1}{2}Y_2\frac{\partial^2 Y_2}{\partial p^2} + \frac{\partial^2 \psi}{\partial p^2}.$$

Now we prove the following lemma.

L e m m a . If a smooth curve $\pi: t \longrightarrow \pi(t)$ is such that $\pi(0) = 0$, and $(d\pi/dt)(0) = B_\pm/A_\pm$ then

(x) $$(\partial v/\partial p)(t,\pi(t)) \sim C\,\frac{1}{t}.$$

P r o o f . First of all we consider the equation $R(t,\pi(t),x_1) = 0$, $R(t,\pi(t),x_1) = \pm x_1^3 4 + 2x_1 t(\beta_1 - \alpha_1\beta_2/\alpha_2) + Dt^2 (\mathrm{mod}\ \mathfrak{m}^3) \subset \mathfrak{m}^2$. The determinant of the Hessian matrix, at zero, of this function is $-(\beta_1 - \alpha_1\beta_2/\alpha_2)^2 < 0$. On the basis of Morse Lemma stating about a normal form of function in a neighbourhood of nondegenerated critical point we get the two solutions of the equation mentioned above, namely the curves: $\gamma_1 : s \longrightarrow (\tau(s), X_1(x)) = (\mp 2\alpha_2/(\beta_1\alpha_2 - \alpha_1\beta_2))s^2 + O(s^3), s)$ and $\gamma_2 : s \longrightarrow (\tau(s), X_1(s)) = (s, (D\alpha_2/2(\beta_2\alpha_1 - \beta_1\alpha_2))s + O(s^2))$, where $R(\tau(s), \pi(\tau(s)), X_1(s)) \underset{s}{\equiv} 0$.

The curve γ_2 has no physical meaning (like the Van der Waals theory). Hence after a study of dependence of (ix) on the curve γ_1 we obtain the thesis of our Lemma, i.e. $\gamma' = 1$.

Let us set in (iv) and (v) $t = 0$. Then by (iv) $p = \pm \frac{4}{\alpha_2} \varphi^3(x_1)$, φ is a smooth function, $\varphi'(0) = 1$, so we obtain $X_1(0,p) = \varphi^{-1}((\pm \frac{\alpha_2}{4} p)^{1/3})$. Substitutating this term to (v) we get $v - v_c \sim (\pm\alpha_2^4/4)^{1/3} . p^{1/3}$, q.e.d.

At once we have also the following corollary.

C o r o l l a r y 5.2. (The law of "rectlinear diameter" [8])

$$(v_G + v_L)(t) = 2v_c + C_1 t + O((t^{1/2})^3), \quad C_1 \text{ is a constant}$$

6. Final remarks

Physical attainability of the above introduced quantities impose some restrictions onto the coefficients of its expansions. The aim of our considerations has been a derivation of critical exponents, hence we omit the problem of above mentioned physical quantities.

We have proposed the general features of a possible approach to critical phenomena. In order to consider the concrete systems the approach must be enriched, for example the symmetry properties of ferromagnet (e.g. uniaxial ferromagnet) defines some constraints on the physically attainable spaces of equilibrium states (cf. [6]). The consequent description, by the singularity theory methods, in different cases, leads to the different mathematical problems and provides and interesting physical conclusions (cf. [6], [5]).

In more complicated cases Theorem 4.3 becomes insufficient and it is necessary to extend it with respect to the dimension (as in [11]) and in the presence of constraints.

The symplectic framework applied to the **composite system** (according to [2]), i.e. the system defined as a conjunction of disjoint subsystems, provides as a conclusion the Maxwell convention. In this way one can obtain the space of coexistence states as in the figure contained in the text*).

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*) The last remark, as a problem, was suggested to me by Prof. W.M.Tulczyjew.

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