

SINGULAR SYMPLECTIC STRUCTURES AND SYMPLECTIC
REDUCTION OF CLASSICAL COMPOSITE SYSTEMS

by

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ABSTRACT.

The geometrical resolution problem for singular lagrangian varieties is formulated and the partial classification of images of lagrangian submanifolds and singular symplectic structures is given. An introductory symplectic framework for extended description of the composite thermodynamical systems is proposed. We explain, using simpler smooth symplectic objects, appearance of singular lagrangian varieties as the models for the real states of physical systems in equilibrium. Thus the Maxwell's convention is obtained as a consequence of the existence of the appropriate symplectic resolution of the system. In the standard singularity theory approach the classification of general constitutive sets is given and the normal forms for the generic singularities of the reduced constitutive sets are described in small dimensions. Using the theory of constitutive sets and their singularities the geometric classification of phase transitions and singular phase diagrams for the classical systems is proved.

1. INTRODUCTION

The simplest problem concerning singular lagrangian varieties is the following resolution problem: Let (P, ω) be a symplectic manifold. Let (P, X, π) be a differential fibration and θ a 1-form on P such that $\omega = d\theta$. The quadruple (P, X, π, θ) is called a special symplectic structure on P if there is a diffeomorphism $\alpha : P \rightarrow T^*X$ such that $\pi = \pi_X \circ \alpha$, $\theta = \alpha^* \theta_X$ (cf. [1], [26]). Let $L \subset (P, \omega)$ be a germ of singular lagrangian variety, i.e. the stratified subset of P the maximal strata of which are lagrangian [22]. The question is: do there exist

- (i) a special symplectic structure (P, X, π, θ) on (P, ω) ,
- (ii) a submersion $\rho : \Lambda \rightarrow X$, for some smooth manifold Λ .
- (iii) a regular (i.e. transversal to the fibres of $T^*\Lambda$, thus generated by a function $F : \Lambda \rightarrow \mathbb{R}$) lagrangian submanifold $N \subseteq (T^*\Lambda, d\theta_\Lambda)$,

such that L is an image of N with respect to the canonical cotangent bundle lifting of ρ , i.e.

$$L = T^*\rho(N) \quad (\text{see } \S 2) \quad .$$

Such problems appear naturally in a study of constitutive sets in mechanics and thermodynamics [24] as well as in the investigations of wave front singularities in the presence of obstacle [3]. Representation of singular equilibrium spaces of states, for various systems encountered in physics, by the corresponding smooth resolutions, bring some light on the geome-

trical structure and the physical sense of these singularities. The corresponding smooth representatives give us the calculational possibility to indicate many universal characteristics (e.g. of the equation of states) for the systems near phase transitions.

Our aim in this paper is to give the postulational basis for resolution of thermodynamical spaces. As the main result we obtain the classification of singular constitutive sets and singular symplectic structures. We also provide the exact resolving procedure for the so-called simple thermodynamical systems, the droplet system and chemical system in the presence of chemical reactions.

In Section 2 we recall the relevant definitions and facts concerning symplectic images as well as we classify the singular symplectic structures. In Sections 3 and 4 we present the geometrical approach to thermodynamical composite systems and discuss qualitative properties of reduced lagrangian varieties as the models of various phenomenological phenomena. In Section 5 we develop the geometry of constitutive sets and provide the classification of their stable images. Direct application of the theory of images of constitutive sets to coexistence of phases is discussed in Section 6. In this section we show how useful the symplectic approach is in understanding quite complicated structure of phase transitions.

§2. SYMPLECTIC IMAGES AND SINGULAR SYMPLECTIC STRUCTURES

Let (P_1, ω_1) and (P_2, ω_2) be two symplectic manifolds (for the basics of symplectic geometry see e.g. [1],[25]). Let $\pi_i : P_1 \times P_2 \rightarrow P_i$ ($i = 1, 2$) be the cartesian projections. We define a symplectic relation R from (P_1, ω_1) to (P_2, ω_2) as an immersed lagrangian submanifold of the symplectic manifold $(P_1 \times P_2, -\pi_1^*\omega_1 + \pi_2^*\omega_2)$ (cf. [6],[25]). Let C be a submanifold of P_1 , let the symplectic relation R be given as a graph of an appropriate differentiable submersion $\pi : C \rightarrow P_2$. Then R is called the reduction relation from (P_1, ω_1) to (P_2, ω_2) (cf. [7], p. 561), and C is a soisotropic submanifold of (P_1, ω_1) , i.e. at each $x \in C$, $(T_x C)^\S \subseteq T_x C$, where $(T_x C)^\S$ is the symplectic polar of $T_x C$ defined by

$$(T_x C)^\S = \left\{ v \in T_x P_1; \langle v \cap u, \omega_1 \rangle = 0 \quad \forall u \in T_x C \right\} \quad (\text{see e.g. [6] p.9}).$$

For any subset $F \subset P_1$, the set $R(F) = \{p_2 \in P_2; \text{there exists } p_1 \in F \text{ such that } (p_1, p_2) \in R\} \subset P_2$ is called the image of F with respect to the relation R . If $S \subset P_2$ then the set ${}^tR(S) \subset P_1$ will be called the counterimage of S with respect to R . Here tR is the transposed relation,

$${}^tR = \left\{ (p_2, p_1) \in P_2 \times P_1; (p_1, p_2) \in R \right\} \subset (P_2 \times P_1, -\pi_1^*\omega_2 + \pi_2^*\omega_1).$$

Most applications of symplectic geometry use the cotangent bundles as the typical examples of symplectic manifolds (cf. [15],[14],[23],[22]). Hence in what follws we deal with symplectic manifolds endowed with the special cotangent bundle structures (cf. [24]).

Now let X and Y be two smooth manifolds and let $f : X \rightarrow Y$ be a smooth mapping. We define the set

$$T^*f = \{ (\xi, \eta) \in T^*X \times T^*Y ; \xi = f^*\eta \} .$$

It is easy to check (see e.g. [26], p.5) that T^*f is a symplectic relation in $(T^*X \times T^*Y, \pi_2^*d\theta_Y - \pi_1^*d\theta_X)$, where θ_X, θ_Y are the Liouville forms corresponding to T^*X and T^*Y respectively (see [1]). This is the graph of symplectomorphism if and only if f is a diffeomorphism.

PROPOSITION 2.1. Let $\rho : X \rightarrow Y$ be a smooth submersion (i.e. $\text{rank } d\rho(x) = \dim Y$ at each $x \in X$). Then the set $T^*\rho \subset (T^*X \times T^*Y, \pi_2^*d\theta_Y - \pi_1^*d\theta_X)$ is the symplectic reduction relation from T^*X to T^*Y .

PROOF. We have the natural mappings associated to ρ (cf. [1]):

$$(*) \quad T^*X \xleftarrow{h} X \times_Y T^*Y \xrightarrow{\tilde{\rho}} T^*Y ,$$

where $\tilde{\rho}$ is the restriction to $X \times_Y T^*Y$ of the projection of $X \times T^*Y$ onto the second factor. Since h is an immersion, we identify $X \times_Y T^*Y$ (the fibre pullback of T^*Y by means of ρ) to its image C in T^*X . It is easy to see that $T^*\rho$ is a symplectic relation (see [6], p.13). Moreover on the basis of (*) we see that $T^*\rho$ is the graph of differentiable submersion $C \rightarrow T^*Y$ (because of ρ is submersion) defined by $\tilde{\rho}$. Hence

$T^*\rho$ is the reduction relation and C is the corresponding coisotropic submanifold of it.

In more general context (see [6]), to each coisotropic submanifold $C \subseteq (T^*X, d\theta_X)$ corresponds the canonical symplectic manifold, defined by the so-called homogeneous system, i.e. the triplet $(T^*X, d\theta_X, C)$ defining the corresponding characteristic distribution on C . If B is the set of its integral manifolds admitting a differentiable structure then there is a unique symplectic structure β on B such that

$$\tilde{\rho}^*\beta - d\theta_X|_C = 0 \quad ,$$

where $\tilde{\rho} : C \rightarrow B$ is the canonical submersion (see [6], p.13).

Let L be a lagrangian submanifold of $(T^*X, d\theta_X)$. The singularity structure of the image of L with respect to the reduction relation $T^*\rho$ depends on the properties of mutual intersection of L and C (here also $C = {}^tT^*\rho(T^*Y)$).

PROPOSITION 2.2. Let $T^*\rho \subseteq (T^*X \times T^*Y, \pi_2^*d\theta_Y - \pi_1^*d\theta_X)$ be the reduction relation (as in Proposition 2.1). Let L be a lagrangian submanifold of $(T^*X, d\theta_X)$ and let C be the above defined coisotropic submanifold of $(T^*X, d\theta_X)$. We assume that $C \cap L$ is smooth and $T(C \cap L) = TC \cap TL$ (clean intersection condition [25]). Then $\tilde{\rho}|_{C \cap L} : C \cap L \rightarrow T^*Y$ (defined in (*)) has a constant rank and $T^*\rho(L)$ is an immersed lagrangian submanifold of $(T^*Y, d\theta_Y)$.

The proof of this proposition follows immediately on the basis of [7] Proposition 2.

Proposition 2.2 is very useful in representing the lagrangian submanifolds in cotangent bundles by the so-called generating families, or Morse families (see [26]). Let $L \subseteq (T^*X, d\theta_X)$ be a lagrangian submanifold generated by a smooth function $F : X \rightarrow \mathbb{R}$, i.e. $dF(X) = L$, $dF : X \rightarrow T^*X$. If L is transversal to $C = {}^t T^*\rho(T^*Y)$ then F is called the Morse family generating of the lagrangian submanifold $T^*\rho(L) \subseteq (T^*Y, d\theta_Y)$. A lagrangian submanifold of a cotangent bundle can always be generated, at least locally, by Morse families (see [26], Lecture 6). If (y, λ) are coordinates of X adapted to the submersion $\rho : X \rightarrow Y$, then the transversality condition for a function $(y, \lambda) \rightarrow F(y, \lambda)$ is formulated as the maximality of the rank of the matrix (cf. [4])

$$\left(\frac{\partial^2 F}{\partial y \partial \lambda}, \frac{\partial^2 F}{\partial \lambda \partial \lambda} \right)$$

In terms of canonical coordinates (y, p) of T^*Y , the lagrangian submanifold $T^*\rho(L)$ is described by equations:

$$p_i = \frac{\partial F}{\partial y_i}(y, \lambda), \quad 0 = \frac{\partial F}{\partial \lambda_j}(y, \lambda), \quad i = 1, \dots, \dim Y, \\ j = 1, \dots, \dim X - \dim Y.$$

There are many examples where the above introduced transversality conditions or clean-intersection conditions are not

fulfilled (see [4], [17], [23]). If this is so the image set $T^*\rho(L)$ is no longer a differential submanifold. The aim of this paper is to describe the fundamental properties of such varieties encountered in classical physics.

EXAMPLE 2.3. ($C \cap L$ is not smooth submanifold of T^*X).

Let $\dim T^*X = 4$ and $(x_1, x_2; \xi_1, \xi_2)$ are coordinates on T^*X . We define $C = \{p \in T^*X; \xi_2 = 0\}$ and $L = dF(X)$, where $F(x_1, x_2) = \frac{1}{4}x_2^4 + \frac{1}{2}x_1x_2^2$. We see that $C \cap L = \left\{ p \in T^*X; \xi_1 - \frac{1}{2}x_2^2 = 0, (x_2^2 + x_1)x_2 = 0, \xi_2 = 0 \right\}$ is not regular. Obviously the reduced set $S = T^*\rho(L)$, where $\rho(x_1, x_2) = x_1$, is not a submanifold of T^*Y .

EXAMPLE 2.4. ($C \cap L$ is a submanifold of T^*X , however $T^*\rho(L)$

is singular). Let $(T^*X, d\theta_X)$ and $C \subseteq T^*X$ be as in Example 2.3,

here $\tilde{\rho}(x_1, x_2, \xi_1) = (x_1, \xi_1)$. Let the generating function for

$L \subseteq (T^*X, d\theta_X)$ has a form $F(x_1, x_2) = \frac{1}{5}x_2^5 - \frac{2}{3}x_1x_2^3 + x_2x_1^2$. In

this case $C \cap L = \left\{ p \in T^*X; \xi_1 - \frac{4}{3}x_2^3 = 0, x_1 - x_2^2 = 0, \xi_2 = 0 \right\}$.

Hence the reduced set $S = T^*\rho(L) = \left\{ (x_1, \xi_1) \in T^*Y; 9\xi_1^2 = 16x_1^3 \right\}$

has the cusp singularity (cf. [20]) at zero. It is easy to check

that $\tilde{\rho}|_{C \cap L}$ has no constant rank in this case, which is a

reason of appearance of this singularity. It also appeared as

a member of the hierarchy of open-swallowtails introduced by

Arnold [4] (cf. [17]).

We generalize now the construction, introduced in [4], which was a part of original motivation for our investigations of singular images of lagrangian submanifolds [17].

Let C, V be two coisotropic submanifolds of a symplectic manifold (P, ω) , $\text{codim } C = \text{codim } V = k$. Let $\pi : C \rightarrow M$ be the canonical characteristic projection. M is the corresponding symplectic manifold, $\dim M = 2n - 2k$, $\dim P = 2n$. Let V and C intersect transversally, so we have the next submanifold $W \subseteq C$, $W = V \cap C$, and its smooth mapping κ onto M , $\kappa = \pi|_W$. As an immediate consequence of this construction we obtain.

PROPOSITION 2.5. The singular generic symplectic structures on W ($\dim W = 2(n-k)$) are classified by classifying smooth mappings $\kappa = \pi|_W$ treated as the mapping diagrams $W \hookrightarrow C \xrightarrow{\pi} M$ (cf. [27]) with $\dim \text{Ker } \kappa_* \leq k$.

COROLLARY 2.6. (cf. [4]). Let $k = 1$, then generically the singular symplectic structures on W , say ω_W , are classified by the following germs of Whitney projections (see [20])

$$\kappa_r(y_0, \dots, y_{r-1}, y_{r+1}, \dots, y_N) = (y_1, \dots, y_{r-1}, y_0^{r+1} + y_1 y_0^{r-1} + \dots + y_{r-1} y_0, y_{r+1}, \dots, y_N)$$

where $\omega_W = \kappa_r^* \omega_M$, $\pi(y_0, \dots, y_N) = (y_1, \dots, y_N)$, $\dim W = N$ and ω_M is the canonical symplectic structure on M . Moreover if $r \leq 3$ ω_W has the corresponding normal forms

$$\underline{r=1} \quad \omega_W = 2p_0 dq_1 \wedge dp_0 + \sum_{i=2}^{n-2} dp_i \wedge dq_i$$

$$\underline{r=2} \quad \omega_W = d(p_0^3 + p_1 p_0) \wedge dp_1 + \sum_{i=2}^{n-2} dp_i \wedge dq_i$$

$$\underline{r=3} \quad \omega_W = dq_2 \wedge d(p_0^4 + p_2 p_0^2 + q_2 p_0) + dp_1 \wedge dq_1 + \sum_{i=3}^{n-2} dp_i \wedge dq_i$$

where $(q_0, \dots, q_n, p_0, \dots, p_n)$ are the corresponding Darboux coordinates on P in which $\pi : C \rightarrow M, \pi(q, \dots, q_n, p_0, \dots, p_n) = (q_1, \dots, q_n, p_1, \dots, p_n)$.

PROOF. On the basis of Whitney's theorem (see [2], p.163), classifying the stable projections $W \hookrightarrow C \xrightarrow{\pi} M$, by an appropriate choice of local coordinates on W, C and M , we can reduce π to the form $\pi(y_0, \dots, y_N) = (y_1, \dots, y_N)$ and $W = \{y \in C; y_0^{r+1} + y_1 y_0^{r-1} + \dots - y_r = 0\}$. Applying [3] (Theorems 1,2,3), for the cases $r = 1, 2, 3$, we can reduce the symplectic forms ω_M, ω by diffeomorphism preserving the corresponding swallowtail to the Darboux normal forms

$$\omega = \sum_{i=0}^n dp_i \wedge dq_i, \omega_M = \sum_{i=1}^n dp_i \wedge dq_i, C = \{(p, q) \in P; q_0 = 0\},$$

where the respective hypersurface W is given in the following form:

$$\underline{r=1} \quad W = \{(p, q) \in C; p_0^2 + p_1 = 0\}$$

$$\underline{r=2} \quad W = \{(p, q) \in C; p_0^3 + p_1 p_0 + q_1 = 0\}$$

$$\underline{r=3} \quad W = \{(p, q) \in C; p_0^4 + p_1 p_0^2 + q_2 p_0 + p_2 = 0\}$$

Taking the appropriate pullbacks $\kappa_V^* \omega_M$ we obtain the results of Corollary 2.6.

The singular symplectic structures (classified in Corollary 2.6) were used in [3] and [4] to indicate the generic

singular lagrangian varieties, so-called open swallowtails, appearing in the variational problem of bypassing of obstacle. The more comprehensive study of these singularities was done in [17].

REMARK 2.7. Let $\dim P = 8$ and $k = 2$, then the generic singular structures ω_W on W are classified by the germs of the following stable mappings (see e.g. [2] p.68)

$$\Sigma^{1,0} : \kappa(y_1, \dots, y_4) = (y_1, y_2, y_3, y_4^2)$$

$$\Sigma^{1,1,0} : \kappa(y_1, \dots, y_4) = (y_1, y_2, y_3, y_1 y_4 + y_4^3)$$

$$\Sigma^{1,1,1,0} : \kappa(y_1, \dots, y_4) = (y_1, y_2, y_3, y_1 y_4 + y_2 y_4^2 + y_4^4)$$

$$\Sigma^{1,1,1,0} : \kappa(y_1, \dots, y_4) = (y_1, y_2, y_3, y_1 y_4 + y_2 y_4^2 + y_3 y_4^3 + y_4^5)$$

$$\Sigma^{2,0} : \kappa(y_1, \dots, y_4) = (y_1, y_2, y_3^2 \pm y_4^2 + y_1 y_3 + y_2 y_4, y_3 y_4)$$

where coordinates $\{y_1, \dots, y_4\}$ are not necessary adapted to the Darboux normal form of the symplectic structure ω_M .

§3. COMPOSITE SYSTEMS AND SYMPLECTIC REDUCTION RELATIONS

Now we consider a simple thermodynamical system (see e.g. [9]), with the chart of extensive variables $\{x_1, \dots, x_n\}$ parametrizing the space of equilibrium states of the system (cf. [16]). Here the x_i symbolize the independent physical quantities, e.g. the internal energy U , the volume V and the mole numbers N_j . Following [16] (cf. [24]) we introduce the phase space of the system as the symplectic manifold $(T^*X, d\theta_X)$, where θ_X is the corresponding form of equilibrium entropy. The space of equilibrium states, say L , of some real system is a lagrangian submanifold of the phase space $(T^*X, d\theta_X)$ (see [24], p.113). Equilibrium entropy S of the system is a generating function of L . This function provides the so-called fundamental equation of the system (e.g. $\bar{S} = S(U, V, N)$ for one-component simple system [9]).

The form of an equilibrium entropy is as follows

$$\theta_X = \sum_i p_i dx_i$$

where p_i are the thermodynamical intensities, e.g. $1/T$, $1/T$, p/T , $-\mu_j/T$ (T - temperature, p - pressure, μ_j - chemical potentials). The corresponding equations of state

$$p_i = \frac{\partial S}{\partial x_i}(x)$$

are determined by the obvious relation.

$$\theta_X|_L = \pi^*dS \quad ,$$

where $\pi = \pi_X|_L$ and $\pi_X : T^*X \rightarrow X$ is the cotangent bundle projection.

In classical thermodynamics (see [9], [19], [18]), the composite system is defined as a conjunction of spatially disjoint volume elements, i.e. isolated subsystems, each of them is characterized by the set of additive (conserved) quantities - extensive parameters. The walls or internal boundaries limiting thermodynamic subsystems are assumed to be restrictive (or non-restrictive) with respect to the transfer of the various quantities. Manipulations by means of the boundary conditions (imposition or relaxation of constraints) are called thermodynamic operations. The thermodynamic processes are defined as transfers of additive invariants between subsystems after the thermodynamic operations. The sequences of thermodynamic operations applied to the starting system is called a thermodynamic deformation (e.g. in chemical systems as an example of thermodynamic deformation we can consider a simple bringing into the system some new chemical constituents).

The phase space of a composite system has a form:

$$\left(\prod_{\varphi} T^*X_{\varphi}, \sum_{\varphi} \pi_{\varphi}^* d\theta_{X_{\varphi}} \right)$$

where $(T^*X_{\varphi}, d\theta_{X_{\varphi}})$ is the phase space for the corresponding isolated subsystem and $\pi_{\varphi} : \prod_b T^*X_b \rightarrow T^*X_{\varphi}$ is the cartesian projection (φ, b , are integers).

Assuming only the thermodynamical interaction between subsystems (cf. [9], [22]), for the total entropy we can write

$$S = \sum_a S_a$$

where S_a is the entropy function for the corresponding subsystem. By a relaxation of constraints we evoke the corresponding thermodynamic process as a transfer of additive invariants between subsystems, thus we have the transition (irreversible in general) from a more constrained state to a less constrained equilibrium. In such thermodynamic processes some previously controlled parameters tend spontaneously to equilibrium values determined mainly by the remaining controlled additive invariants.

EXAMPLE 3.1. Let us consider the class of thermodynamic deformations of the simple one-component system onto two spatially disjoint isolated subsystems. The corresponding phase space of this composite system is following

$$(T^*X_1 \times T^*X_2, \pi_1^* d\theta_{X_1} + \pi_2^* d\theta_{X_2} = d\theta), \quad \pi_i : T^*X_1 \times T^*X_2 \rightarrow T^*X_i, \quad ,$$

where in the respective local coordinates we have

$$\theta = \frac{1}{T_1} dU_1 + \frac{1}{T_2} dU_2 + \frac{P_1}{T_1} dV_1 + \frac{P_2}{T_2} dV_2 - \frac{\mu_1}{T_1} dN_1 - \frac{\mu_2}{T_2} dN_2$$

$$T^*X_i : \{U_i, V_i, N_i, 1/T_i, P_i/T_i, -\mu_i/T_i\} ; X_i : \{U_i, V_i, N_i\} , \quad (i = 1, 2) .$$

By removing the thermal constraint between subsystems the new controlled extensive variables space is as follows

$$Y ; \{U, V_1, V_2, N_1, N_2\} , \text{ where } U = U_1 + U_2$$

(see e.g. [9]) and the possible range for the spontaneous changes of extensive parameters is defined by the submersion:

$$\rho : X_1 \times X_2 \longrightarrow Y , \rho(U_1, U_2, V_1, V_2, N_1, N_2) = (U_1 + U_2, V_1, V_2, N_1, N_2) .$$

It is easy to check that the corresponding coisotropic submanifold of $T^*X_1 \times T^*X_2$ defined by the symplectic relation

$$T^*\rho \subseteq (T^*(X_1 \times X_2) \times T^*Y , \pi_2^*\omega_Y - \pi_1^*\omega_{X_1 \times X_2})$$

has a form

$${}^t_{T^*\rho}(T^*Y) = C = \{p \in T^*X_1 \times T^*X_2 ; T_1 = T_2\} .$$

Hence, this example suggests that in general thermodynamical context equilibrium condition has the structure of coisotropic submanifold. We can formulate the following

HYPOTHESIS 3.2. Equilibrium of a thermodynamical system subjected to the class of deformations is determined by the corresponding reduction relation

$$T^*\rho \subseteq (T^*X \times T^*Y , \pi_2^*\omega_Y - \pi_1^*\omega_X) ,$$

where $\rho : X \rightarrow Y$ is a submersion defining the control variables, and (T^*X, ω_X) is a phase space corresponding to the intermediate composite system.

The coisotropic submanifold $C = {}^tT^*\rho(T^*Y) \subseteq (T^*X, \omega_X)$ is called the condition of equilibrium with respect to the imposed class of thermodynamic deformations.

REMARK 3.3. Thermodynamic processes caused by the thermodynamic operations are irreversible, so one can generalize the above introduced notions to the irreversible thermodynamics framework. However in this paper we consider the transition from the more constrained to a less constrained equilibrium (cf. [9]) and we deal only with the initial and final equilibrium states (the initial lagrangian submanifold and the reduced lagrangian submanifold respectively), ignoring both intermediate non-equilibrium situations and also the time delay involved in the transitions.

EXAMPLE 3.1. (continuation) In the standard composite system (see Fig. 1), by removing all constraints, we can control the total sums of the corresponding additive extensive invariants, i.e. the submersion $\rho : X \rightarrow Y$ is as follows (system composed of k -subsystems)

$$\rho(U_1, \dots, U_k, V_1, \dots, V_k, N_1, \dots, N_k) = (\Sigma_i U_i, \Sigma_i V_i, \Sigma_i N_i) \quad .$$

Hence, the corresponding reduction relation

$$T^*p = \left\{ \left(\left(U_i, V_i, N_i; \frac{1}{T_i}, \frac{P_i}{T_i}, \frac{-\mu_i}{T_i} \right) \cdot \left(U, V, N; \frac{1}{T}, \frac{P}{T}, \frac{-\mu}{T} \right) \right) \in T^*X \times T^*Y ; \right.$$

$$U = \sum_i U_i, V = \sum_i V_i, N = \sum_i N_i, \frac{1}{T_i} = \frac{1}{T}, \frac{P_i}{T_i} = \frac{P}{T}, \frac{\mu_i}{T_i} = \frac{\mu}{T}, i = 1, \dots, k \} .$$

and the equilibrium condition (cf. [18], [9] and Prop.2.1) is as follows

$$C = \left\{ \left(U_i, V_i, N_i; \frac{1}{T_i}, \frac{P_i}{T_i}, \frac{-\mu_i}{T_i} \right) \in T^*X; T_i = T_j, P_i = P_j, \mu_i = \mu_j, 1 \leq i, j \leq k \right\} .$$

EXAMPLE 3.4. (Droplet equilibrium). Let us look at the droplet in some surrounding gas as a composite system. The corresponding phase space $(T^*X, d\theta_X)$ can be characterized as follows

$$\theta_X = \frac{1}{T_1} dU_1 + \frac{1}{T_2} dU_2 + \frac{P_1}{T_1} dV_1 + \frac{P_2}{T_2} dV_2 - \frac{\mu_1}{T_1} dN_1 - \frac{\mu_2}{T_2} dN_2 - \beta d\sigma$$

where σ is an area of the droplet (see Fig. 2) and

$\{U_1, U_2, V_1, V_2, N_1, N_2, \sigma\}$ are the standard coordinates of X . The natural submersion meddelling the equilibrium of the droplet has a form

$$\rho \left(U_1, U_2, V_1, V_2, N_1, N_2, \sigma \right) |_{\{g=0\}} = \left(U_1 + U_2, V_1 + V_2, N_1 + N_2 \right)$$

where $g : X \rightarrow \mathbf{R}$ is the function of a possible dependence of σ on the rest of extensive variables. We can assume that g depends only on two variables, say σ and V_1 (volume of the droplet).

By simple calculations using the local coordinates we obtain the corresponding equilibrium condition:

$$C = \left\{ \left(U_1, U_2, V_1, V_2, N_1, N_2, \sigma, \frac{1}{T_1}, \frac{1}{T_2}, \frac{P_1}{T_1}, \frac{P_2}{T_2}, \frac{-\mu_1}{T_1}, \frac{-\mu_2}{T_2}, -\beta \right) \in T^*X ; \right. \\ \left. T_1 = T_2, \mu_1 = \mu_2, \frac{P_1}{T_1} = \frac{P_2}{T_2} + \frac{\partial g}{\partial V_1}(\sigma, V_1) a, -\beta = \frac{\partial g}{\partial \sigma}(\sigma, V_1) a, a \in \mathbf{R} \right\} .$$

This is equivalent to the equation

$$P_1 - P_2 = -\alpha \frac{\partial g}{\partial V_1}(\sigma, V_1) / \frac{\partial g}{\partial \sigma}(\sigma, V_1) = \alpha \frac{d\sigma}{dV_1} \Big|_{g(\sigma, V_1) = 0} ,$$

where $\alpha = \beta T$ is a surface tension of the droplet (cf.[18]). In this example we used a little more general notion of reduction, namely the reduction relation with constraint. In what follows we give the precise description of such objects.

REMARK 3.5. In the standard phase space of thermodynamics (let us take the internal energy representation [24], [9])

$(T^*Q_1, d\theta_{Q_1})$, $T^*Q_1 : \{S, V, N, T, -p, \mu\}$, $\theta_{Q_1} = TdS - pdV + \mu dN$, there is an additional structure, namely the structure defined by the so-called Gibbs-Duhem distribution $\Gamma = \{\chi = 0\}$, where $\chi = -SdT + Vdp - Nd\mu$. This distribution is not integrable (it is easy to check that $\chi \cap d\chi \neq 0$ on T^*Q_1). However every tangent hyperplane $\Gamma_p \subset T_p T^*Q_1$ is a coisotropic subspace, so taking the symplectic polar Γ_p^S to every Γ_p we obtain the corresponding characteristic distribution Γ^S (see §2). Γ^S is one dimensional and integrable, $\Gamma^S = \left\{ \delta S \frac{\partial}{\partial S} + \delta V \frac{\partial}{\partial V} + \delta N \frac{\partial}{\partial N} ; N\delta S + S\delta N = 0 \text{ and } N\delta V = V\delta N \right\}$. The space of equilibrium

states of the system is a lagrangian submanifold $L \subseteq (T^*Q_1, d\theta_{Q_1})$ such that $TL \subset \Gamma$. Let $F : Q_1 \rightarrow \mathbf{R}$ be a generating function for L and $i : L \rightarrow T^*Q_1$ its immersion. Let us define the following function $G : T^*Q_1 \rightarrow \mathbf{R}$, $G(S, V, N, T, p, \mu) = TS - pV + \mu N$. The condition $TL \subset \Gamma$ implies

$$i^*dG = TdS - pdV + \mu dN + SdT - Vdp + Nd\mu \Big|_{L = \theta_{Q_1}} \Big|_{L} - \chi \Big|_{L} = dP$$

and the corresponding Euler equation for F .

$$i^*G = \pi_{Q_1} \Big|_{L}^* F$$

(cf. [9], [19]).

4. REDUCED SPACE OF EQUILIBRIUM STATES.

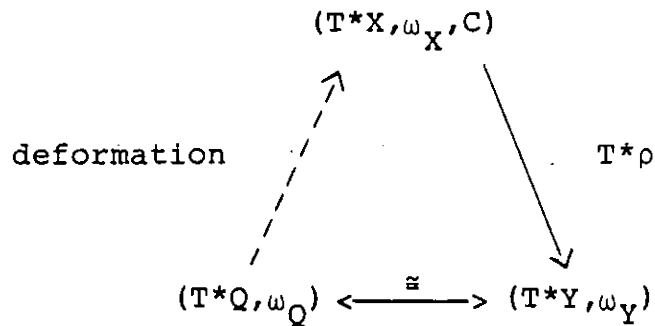
By Hypothesis 3.2. the symplectic reduction relation describes the corresponding process of establishing of equilibrium in deformed systems. Let $L \subseteq (T^*Q, \omega_Q)$ be a space of equilibrium states of a thermodynamical system endowed with the phase space (T^*Q, ω_Q) :

HYPOTHESIS 4.1. Let the assumptions of Hypothesis 3.2. be fulfilled. Let the lagrangian submanifold $\tilde{L} \subseteq (T^*X, \omega_X)$ represents the space of equilibrium states of the composite system corresponding to the considered class of deformations of the initial system $L \subseteq (T^*Q, \omega_Q)$. Then the space of equilibrium states of the deformed equilibrium system $W \subseteq (T^*Y, \omega_Y)$ is represented as a symplectic image ; i.e.

$$W = T^*\rho(\tilde{L}) \quad .$$

The thermodynamical phenomena do not suggest in general any regular intersection condition between the lagrangian submanifold $\tilde{L} \subseteq (T^*X, \omega_X)$ and the corresponding equilibrium condition $C \subseteq (T^*X, \omega_X)$ (see Hypothesis 3.2). Hence the space of equilibrium states of the deformed system can be very complicated and not smooth in general (see Fig. 3.). Our aim in this paper is to give the geometrical framework adapted to the canonical representation of the singular constitutive sets by their smooth resolutions (cf. [17]).

If we assume that the reduced phase space is isomorphic to the phase space of the initial perfect system, i.e. we have the following diagram



Then the stability notion of the initial space of equilibrium states $L \subseteq (T^*Q, \omega_Q)$ can be defined.

DEFINITION 4.2. Let $L \subseteq (T^*Q, \omega_Q)$ be a space of equilibrium states of the system. We say that L is stable with respect to the given group of deformations if and only if L and $T^*\rho(\tilde{L})$ are isomorphic, i.e. there exists a symplectomorphism $\varphi : (T^*Q, \omega_Q) \rightarrow (T^*Y, \omega_Y)$ such that

$$\varphi(L) = T^*\rho(\tilde{L})$$

where \tilde{L} and ρ were defined before and are determined by the class of deformations.

As an example of the unstable space of equilibrium states we take the smooth surface given by the Van der Waals equation (see [15], [9]). The stabilization of this space (near critical points) with respect to the standard deformations into two

thermodynamically interacting subsystems corresponds exactly to the so-called Maxwell convention. The stabilized space is no longer smooth (see Fig. 3.). Because of the universality of this example we give its more precise formulation.

Let us continue Example 3.1. In the first step we assume for simplicity that the constraint separating the corresponding two subsystems is diathermic (cf. [9]). This suggests the use of Helmholtz cotangent bundle structure (special symplectic structure [24]) for the phase space of the system i.e.

$T^*Q : \{T, V, N; -S, -p, \mu\}$, $\theta_Q = -SdT - pdV + \mu dN$. The corresponding condition of thermol equilibrium in $(T^*Q_1 + T^*Q_2, \pi_1^*d\theta_{Q_1} + \pi_2^*d\theta_{Q_2})$ has a form (see Example 3.1.)

$$C_T = \left\{ \left(T_1, V_1, N_1, T_2, V_2, N_2; -S_1, -p_1, \mu_1, -S_2, -p_2, \mu_2 \right) \in T^*(Q_1 \times Q_2); T_1 = T_2 = T \right\} .$$

Since the phase transitions are isobaric and isothermic processes it is reasonable to fix one of the intensive parameters, say T , and localize the other one (p) in the point of phase transition. In what follows we use the proposed geometric view point to describe formally some aspects of phase transitions (see [21], [19]).

We see that the space of characteristics of C_T is canonically isomorphic to $(T^*X, d\theta_X)$ where X is an open subset of \mathbb{R}^5 with local chart $\{T, V_1, V_2, N_1, N_2\}$ and $\theta_X = -SdT - p_1dV_1 - p_2dV_2 + \mu_1dN_1 + \mu_2dN_2$, where $S = S_1 + S_2$. The corresponding submersion $\tilde{\rho} : C_T \rightarrow T^*X$ defined in §2 is as follows:

$$\begin{aligned} \tilde{\rho} \left(T, V_1, N_1, T, V_2, N_2, -S_1, -p_1, \mu_1, -S_2, -p_2, \mu_2 \right) &= \\ &= \left(T, V_1, V_2, N_1, N_2, - (S_1 + S_2), -p_1, -p_2, \mu_1, \mu_2 \right) . \end{aligned}$$

Let the space of equilibrium states $L \subseteq (T^*Q, d\theta_Q)$ be defined by the Helmholtz free energy function $F : Q \rightarrow \mathbb{R}$ (cf. [24], p.113). Then the corresponding generating function for lagrangian submanifold $\tilde{L} \subseteq (T^*X, d\theta_X)$ representing the equilibrium states of the composite system (with respect to the considered class of deformations) has a form

$$\tilde{F} \left(T, V_1, V_2, N_1, N_2 \right) = F \left(T, V_1, N_1 \right) + F \left(T, V_2, N_2 \right) ,$$

since the two subsystems have the same nature.

The submersion ρ (cf. Hypothesis 3.2) for the full contact of subsystems is as follows:

$$\rho : X \rightarrow Y, \rho \left(T, V_1, V_2, N_1, N_2 \right) = \left(T, V_1 + V_2, N_1 + N_2 \right)$$

and the corresponding equilibrium condition

$$C = \left\{ \left(T, V_1, V_2, N_1, N_2, -S, -p_1, -p_2, \mu_1, \mu_2 \right) \in T^*X; p_1 = p_2, \mu_1 = \mu_2 \right\} .$$

We see that $(T^*Q, d\theta_Q) \cong (T^*Y, d\theta_Y)$ so we can ask for the stability of the considered space of equilibrium states L . To give an answer to this question we must look at the image of lagrangian submanifold $\tilde{L} \subseteq (T^*X, d\theta_X)$ with respect to the symplectic relation $T^*\rho \subseteq (T^*X \times T^*Y, \pi_2^*d\theta_Y - \pi_1^*d\theta_X)$.

Let us consider the Van der Waals system (see [9]) in the neighbourhood of critical point (cf. [21]) or the system with the space of equilibrium states of type A_3 (cf. [16], [8], [10]). Let us fix the total number of moles, i.e. $N = \text{const.}$, so we have now the new parametrization for Q , $Q : \{T, V\}$ and respectively $T^*Q : \{T, V; -S, -p\}$, $d\theta_Q = -pdV - SdT$.
 $X := \{(T, V_1, V_2, N_1, N_2) ; N_1 + N_2 = \text{const.}\}$.
 $\rho(T, V_1, V_2, N_1, N_2) = (T, V_1 + V_2)$. By simple calculations, using the standard formula (cf. [24], [5]) and Proposition 2.1. we obtain

PROPOSITION 4.3. For the class of deformations of the system onto two isolated subsystems the corresponding image $T^*\rho(\tilde{L})$ is described by the following equations

$$\begin{aligned} (1) \quad -p &= \frac{\partial}{\partial V} F(T, V - V_1, N - N_1) \\ (2) \quad -S &= \frac{\partial F}{\partial T}(T, V_1, N_1) + \frac{\partial F}{\partial T}(T, V - V_1, N - N_1) \\ (3) \quad 0 &= \frac{\partial}{\partial V_1} (F(T, V_1, N_1) + F(T, V - V_1, N - N_1)) \\ (4) \quad 0 &= \frac{\partial}{\partial N_1} (F(T, V_1, N_1) + F(T, V - V_1, N - N_1)) \end{aligned}$$

PROOF. It is easy to check that the image of \tilde{L} with respect to $T^*\rho$ is described by the following equation

$$-pdV - SdT = d\left(F(T, V_1, N_1) + F(T, V - V_1, N - N_1)\right)$$

which implies the equations of Proposition 4.3.

F is a homogeneous function (with respect to the extensive variables - Gibbs-Duhem equation [9] and Remark 3.5.). Thus we can write

$$(5) \quad F(T, V_i, N_i) = N_i f(T, v_i), \quad v_i = V_i/N_i, \quad i = 1, 2$$

where f is a differentiable function. We immediately have

COROLLARY 4.4. Let us assume the homogeneity property (5) for the function F . Then the equations (3), (4), in terms of function f , can be rewritten in the following form:

$$(6) \quad \frac{\partial f}{\partial v}(T, v_1) = \frac{\partial f}{\partial v}(T, v_2) \quad ,$$

$$(7) \quad f(T, v_1) - v_1 \frac{\partial f}{\partial v}(T, v_1) = f(T, v_2) - v_2 \frac{\partial f}{\partial v}(T, v_2) \quad .$$

Let us fix T . By M we denote the set of pairs $(v_1, v_2) \in \mathbf{R}^2$ such that (6), (7) are fulfilled. We denote $\Delta = \{(v_1, v_2) \in \mathbf{R}^2; v_1 = v_2\}$, thus $M \setminus \Delta$ we call the set of Maxwell points. Obviously, the pairs $(v_1, v_2) \in \Delta$ are solutions to equations (6) and (7). This implies that the initial space L is contained in the corresponding reduced space $T^*_\rho(\tilde{L})$.

By simple reformulation of Corollary 4.4. we obtain

COROLLARY 4.5. The following conditions are equivalent

(a) $(v_1, v_2) \in M \setminus \Delta$

(b) $\int_{v_1}^{v_2} \left(\frac{\partial f}{\partial v}(T, v) - \frac{\partial f}{\partial v}(T, v_1) \right) dv = 0$ and $\frac{\partial f}{\partial v}(T, v_1) - \frac{\partial f}{\partial v}(T, v_2) = 0$.

Let us notice that the condition (6) in Corollary 4.5 is equivalent to the condition of equal areas $(\sigma_1 = \sigma_2)$ introduced by Maxwell [9] for the Van der Waals gas (see Fig. 3.). So the method of stabilizing of L give us the space of equilibrium states endowed with the Maxwell's additional part.

For the Van der Waals system we have

(8) $f(T, v) = C_v T \ln \frac{eK}{RT} - RT \ln (v-b) - \frac{a}{v}$

(cf. [9]).

PROPOSITION 4.6. Let the function f have a form (8) and the assumptions of Proposition 4.3. are fulfilled. Then in the neighbourhood of critical point (of the Van der Waals system) we have

$$T^* \rho(\tilde{L}) = L_1 \cup L_2 ,$$

and the smooth components L_1, L_2 have the following form

$$L_1 : (-S, -p) = \left(N \ln \left(\frac{eK}{RT} \right)^{C_v} \frac{1}{(V/N-b)^R}, \frac{dN^2}{V^2} - \frac{RTN}{V-bN} \right)$$

$$L_2 : (-S, -p) = \left(\frac{V-v_2 N}{v_1-v_2} \ln \left(\frac{eK}{RT} \right)^{C_v} \frac{1}{(v_1-b)^R} + \frac{V-v_1 N}{v_2-v_1} \ln \left(\frac{eK}{RT} \right)^{C_v} \frac{1}{(v_2-b)^R}, \frac{a}{v_1^2} - \frac{RT}{v_1-b} \right)$$

for $v_1 N < V < v_2 N$, $T < T_C = \frac{8a}{27Rb}$

where (v_1, v_2) is a Maxwell point depending on T (see Fig. 3.).

PROOF. Using Proposition 4.3., Corollary 4.5. and the form (8) of function f after straightforward calculations we obtain the desired structure of $T^*\rho(\tilde{L})$ (cf. [15]).

REMARK 4.7. The component L_1 (see Fig. 3.) of $T^*\rho(\tilde{L})$ represents the standard homogeneous states of matter (stable gas and stable liquid, and metastable respectively). However L_2 describes the equilibrium space of coexistence states (coexistence of liquid and gas phases [19]) and has the structure of constrained lagrangian submanifold (for definition see [24], p.103) defined over the constraining variety representing the corresponding phase diagram. The classification of such spaces of coexistence states can be found in [15]. As an immediate consequence of Proposition 4.7. we have the Clapeyron-Clausius equation (cf. [9]) representing the relation between the slope of phase diagram and affine parameters of the line of coexisting states:

$$\frac{dp}{dT}(T) = \frac{s_1(T) - s_2(T)}{v_1(T) - v_2(T)}$$

where $(v_1(T), v_2(T))$ is the Maxwell point corresponding to temperature T , and $s_i(T) = \partial f / \partial T(T, v_i(T))$, $i = 1, 2$.

EXAMPLE 3.4. (continuation) Let us consider the virtual droplets in the Van der Waals gas. The corresponding phase space of the

composite system in thermal equilibrium has a form

$$(T^*X, d\theta_X) ; \theta_X = -SdT - p_1 dV_1 - p_2 dV_2 + \mu_1 dN_1 + \mu_2 dN_2 + \alpha d\sigma \quad \text{and} \\ \{T, V_1, V_2, N_1, N_2, \sigma\} \quad \text{are local coordinates of } X \quad (\text{cf. [18]}).$$

Let us assume the spherical shape of the droplet, i.e. $g = \sigma^3 - 36\pi V_1^2$. The corresponding submersion ρ (with constraints) defining equilibrium of the reduced system is as follows

$$\rho(T, V_1, V_2, N_1, N_2, \sigma) \left\{ \begin{array}{l} N_1 + N_2 = N = \text{const.} = (T, V_1 + V_2) \\ \sigma^3 - 36\pi V_1^2 = 0 \end{array} \right. ,$$

and the generating function for the space of equilibrium states of the composite system $\tilde{L} \subseteq (T^*X, d\theta_X)$ has a standard form (cf. [18]).

$$F(T, V_1, V_2, N_1, N_2, \sigma) = N_1 f(T, V_1/N_1) + N_2 f(T, V_2/N_2) + \alpha \sigma .$$

It is easy to check, that the equations defining $T^*\rho(\tilde{L}) \subset T^*Y$ can be written as follows

$$(9) \quad f(T, v_1) - v_1 \frac{\partial f}{\partial v}(T, v_1) = f(T, v_2) - v_2 \frac{\partial f}{\partial v}(T, v_2)$$

$$(10) \quad p_2 - p_1 = + \frac{\partial f}{\partial v}(T, v_1) - \frac{\partial f}{\partial v}(T, v_2) = - \frac{2\alpha}{r} , \quad v_i = V_i/N_i , \quad i = 1, 2$$

$$S = - \frac{\partial}{\partial T} F(T, V_1, V_2, N_1, N_2, \sigma)$$

$$p = p_2$$

$$V = V_1 + V_2$$

$$N = N_1 + N_2 = \text{const.}$$

$$\sigma^3 - 36\pi V_1^2 = 0$$

where we assumed, $V_1 = \frac{4}{3} \pi r^3$, $\sigma = 4 \pi r^2$, $r > 0$. It is obvious that the equations (9), (10) can be rewritten in the following way

$$(11) \quad \int_{v_1}^{v_2} \left(\frac{\partial f}{\partial v}(T, v) - \frac{\partial f}{\partial v}(T, v_1) \right) dv = v_2 \frac{2\alpha}{r}$$

$$(12) \quad \frac{\partial f}{\partial v}(T, v_2) = \frac{\partial f}{\partial v}(T, v_1) + \frac{2\alpha}{r}, \quad \alpha \geq 0$$

(see e.g. [18]). But these two equations have very convenient geometrical interpretations (see Fig. 4.).

Following Widom [28] we can assume in the critical region

$$(13) \quad \alpha(T) \sim (T - T_c)^\mu, \quad ,$$

where μ is the corresponding critical exponent (cf. [21]).

For the general A_3 model (cf. [16]) we can derive the asymptotic behaviour for minimal radius R_{\min} of an equilibrium droplet near a critical point.

$$(14) \quad R_{\min} \sim 2v_1 \alpha / \int \left(\frac{\partial f}{\partial v}(T, v) - \frac{\partial f}{\partial v}(T, v_2) \right) dv \sim (T - T_c)^{\mu-2} .$$

By the scaling argument (see e.g. [21], [28]) we can obtain an appropriate value for the critical exponent μ using the scaling relations

$$\mu + \nu = \gamma + 2\beta, \quad S\nu = \gamma + 2\beta$$

where ν, γ, β are standard critical exponents (cf. [21]) and S is a dimensionality of the system.

The measured value $\mu = 1.28 \pm 0.06$ is a realistic estimate for μ which is believed to be universal (see [21]). Thus we can deduce from (14) that in the critical region only fluctuations of density exist and any new phase can appear.

§5. THE GEOMETRY OF CONSTITUTIVE SETS

The space of equilibrium states for the system introduced in the preceding section, is a particular case of the so-called constitutive set the notion coming from the control theory of static mechanical systems (cf. [23]).

Let K be an arbitrary subset of the manifold X . We assume K to be semialgebraic (cf. [12]). Let us consider the set of partially ordered subdivisions of K onto disjoint union of semialgebraic components (see [13]). As an example of such subdivision one can take the standard stratification (into smooth submanifolds) which always exists for semialgebraic sets (see [13], [2]).

Let ξ be a subdivision of $K \subset X$, say $K = \bigcup_{i \in I} K_i$. We define the subset TK_i of TX by

$$TK_i = \left\{ v \in TX ; \text{there exists an integral curve } \gamma : \mathbb{R} \rightarrow X \right. \\ \left. \text{for } v \text{ such that } \gamma([0, \varepsilon[) \subset K_i, \text{ for some } \varepsilon > 0 \right\} .$$

So the corresponding tangent space of K subordinate to the subdivision ξ is defined as follows

$$T_{(\xi)} K = \bigcup_{i \in I} TK_i .$$

For the trivial one-component subdivision of K we use also notation TK . For the constraints we write (K, ξ) .

The constitutive set of a system, endowed with the phase space $(T^*X, d\theta_X)$, i.e. the set of points in T^*X defining certain "external forces" (cf. [23]) under which the system will remain in equilibrium, is defined as follows:

$$(15) \quad S = \left\{ p \in T^*X ; \pi_X(p) \in K, \langle v, p \rangle \leq \langle v, \sigma \rangle \quad \text{for each} \right. \\ \left. v \in T_{(\xi)}K \quad \text{such that} \quad \tau_X(v) = \pi_X(p) \right\}$$

where $\sigma : X \rightarrow T^*X$ is a 1-form (defining the regular system before the constraints K are imposed [23]), and S is called the constitutive set corresponding to the subdivision ξ .

EXAMPLE 5.1. Let a material point move freely on the line. Two stops restrict the movements of the point to the interval $-a \leq x \leq a$, $a > 0$. It is easy to check that the constitutive set corresponding to the trivial subdivision is described by

$$\begin{aligned} |x| &\leq a \\ f &= 0 \quad \text{if} \quad |x| < a \\ f &\leq 0 \quad \text{if} \quad x = -a \\ f &\geq 0 \quad \text{if} \quad x = a \end{aligned} ,$$

where (x, f) are coordinates of $T^*X \cong \mathbb{R}^2$.

If (K, ξ) represents the physical constraints imposed on the system with internal energy $U : X \rightarrow \mathbb{R}$. Then the corresponding constitutive set S of the constrained system is defined by the variational principle (15) with $\sigma = dU$. This

principle is the generalization of the principle

$$S' = \left\{ p \in T^*X ; \pi_X(p) \in K , \langle v, p \rangle = \langle v, dU \rangle \text{ for each } v \in TK \text{ such that } \tau_X(v) = \pi_X(p) \right\}$$

valid for the constraint represented by a smooth submanifold $K \subset X$ without boundary.

Let $\rho : X \rightarrow Y$ be a submersion, let $K \subset X$ be a semi-algebraic subset of X , thus described by a number of polynomial equations and inequalities $g_i(x) = 0$, $g_j(x) \leq 0$.

DEFINITION 5.2. The subset $\tilde{S} \subset (T^*Y, d\theta_Y)$ defined as follows

$$\tilde{S} = \left\{ p \in T^*Y ; \pi_Y(p) \in \rho(K) , \langle T\rho(v), p \rangle \leq \langle v, \sigma \rangle \text{ for each } v \in T_{(\xi)}K \text{ such that } \rho(\tau_X(v)) = \pi_Y(p) \right\}$$

is called the reduced constitutive set. We denote it also by $T^*\rho_K(\alpha)_{(\xi)}$ (where $\sigma : X \rightarrow T^*X$ is the one-form). Usually the subdivision of $\rho(K) \subset Y$ is determined by the structure of this reduction procedure.

EXAMPLE 5.3. A freely moving material point on the plane $\mathbb{R}^2, (x, y)$, confined to the parabole $\{y - x^2 = 0\}$ with "y" only the controlled variable can be described as a reduced constitutive set. Here we have

$$\rho(x, y) = y , K = \{y - x^2 = 0\} \text{ (with trivial subdivision)} ; \sigma \equiv 0$$

and \tilde{S} is described by the following conditions

$$\begin{aligned} y &\geq 0 \\ f &= 0 \quad \text{if} \quad y > 0 \\ f &\in \mathbb{R} \quad \text{if} \quad y = 0 \quad , \quad (y, f) \in T^*Y \quad . \end{aligned}$$

We see that this is the constitutive set over $\rho(K) = \{y \geq 0\}$ corresponding to the natural subdivision $\rho(K) = \{y = 0\} \cup \{y > 0\}$.

If the constraint $K \subset X$ is a smooth hypersurface then the local singularities of the constitutive set \tilde{S} are determined by the mutual position of K and fibres of the fibre-map $\rho : X \rightarrow Y$.

The constitutive set (15) with $\sigma \equiv 0$ we call the free constitutive set. The free constitutive sets are responsible for the equilibrium configurations governed by the constraints and they determine the structure of singularities in the presence of internal forces ($\sigma \neq 0$). Now we provide their stable reduced types (for the definitions see [20]).

PROPOSITION 5.4. Let $\dim X - 1 = \dim Y = n$, $K \subset X$, $\text{codim } K = 1$, and let $\rho : X \rightarrow Y$ be a submersion. For the generic, reduced free constitutive set \tilde{S} , around each point $x \in K$ and around the corresponding point $\rho(x) \in Y$ we can choose the local coordinates in which \tilde{S} can be reduced to one from the following normal forms

$$\tilde{S}_k = \left\{ (f, y) \in T^*Y ; \exists_{x_0 \in \mathbb{R}} \text{ such that } x_0^{k+1} + y_1 x_0^{k-1} + \dots + y_{k-1} x_0 - y_k = 0 \right\}$$

$$\sum_{i=1}^n v_i f_i \leq 0 \quad \text{for each } (v_0, \dots, v_n) \in \mathbb{R}^{n+1} \text{ such that}$$

$$v_0 \left((k+1)x_0^k + (k-1)y_1 x_0^{k-2} + \dots + y_{k-1} \right) + \sum_{i=1}^{k-1} x_0^{k-i} v_i - v_k = 0 \left\}$$

where $k \in \mathbb{N}$, $k \leq n$.

PROOF. For the mapping diagrams of type

$$(*) \quad K \hookrightarrow X \xrightarrow{\rho} Y$$

with the standard equivalence relation (see [2]p.175)

$$\begin{array}{ccccc} K & \hookrightarrow & X & \xrightarrow{\rho} & Y \\ \varphi_1 \downarrow & & \downarrow & \varphi_2 & \downarrow & \varphi_3 \\ K & \hookrightarrow & X & \xrightarrow{\rho'} & Y \end{array}, \quad \varphi_i - \text{diffeomorphism } (i=1,2,3)$$

we have the Whitney classification theorem (see [27]). According to this theorem the generic mapping diagram (*) with K-hypersurface and ρ -submersion with one-dimensional fibres, is locally equivalent to one of the following normal forms:

$$\begin{aligned} \rho(x_0, x_1, \dots, x_n) &= (x_1, \dots, x_n) \in Y \\ K &= \left\{ (x_0, x_1, \dots, x_n) \in X ; x_0^{k+1} + x_1 x_0^{k-1} + \dots + x_k = 0 \right\} \end{aligned}$$

where $k = 0, \dots, n$.

Inserting this local expressions into the formula of Definition 5.2, after straightforward calculations we obtain the thesis of Proposition 5.4.

If $\dim Y = n \leq 3$ we can obtain even more, namely the classification of normal forms for the generic images $T^*\rho_K(dF)$.

PROPOSITION 5.5. Let the assumptions of Proposition 5.4. be valid. Let $\dim Y = n \leq 3$. Then for the generic constitutive set $\tilde{S} = T^*\rho_K(dF)$, the corresponding germ of \tilde{S} for every point $p \in \tilde{S}$ is equivalent to one, represented by ρ, K, F , from the following list:

	$\rho : X \rightarrow Y$	$K \subseteq X$	$F : X \rightarrow \mathbb{R}$
1	$(x_0, x_1) \rightarrow x_1$ $(x_0, x_1) \rightarrow x_1$	$\{x_0=0\}$ $\{x_0^2 - x_1 = 0\}$	$x_1 \pm x_1^2$ $x_0 + \rho_1(x_0^2)$
2	$(x_0, x_1, x_2) \rightarrow (x_1, x_2)$ $(x_0, x_1, x_2) \rightarrow (x_1, x_2)$ $(x_0, x_1, x_2) \rightarrow (x_1, x_2)$	$\{x_0=0\}$ $\{x_0^2 - x_1 = 0\}$ $\{x_0^3 + x_0 x_2 - x_1 = 0\}$	$x_1, \pm x_1^2 \pm x_2^2$ $x_2 + x_0, \pm x_2^2 + x_0, x_2 + x_0^3 \pm x_2 x_0$ $\pm x_0 + \rho_2(x_0^3 + x_0 x_2, x_2)$
3	$(x_0, x_1, x_2, x_3) \rightarrow (x_1, x_2, x_3)$ $(x_0, x_1, x_2, x_3) \rightarrow (x_1, x_2, x_3)$ $(x_0, x_1, x_2, x_3) \rightarrow (x_1, x_2, x_3)$ $(x_0, x_1, x_2, x_3) \rightarrow (x_1, x_2, x_3)$	$\{x_0=0\}$ $\{x_0^2 - x_1 = 0\}$ $\{x_0^3 + x_0 x_2 - x_1 = 0\}$ $\{x_0^4 + x_0^2 x_2 + x_0 x_3 - x_1 = 0\}$	$x_1, \pm x_1^2, x_2^2 \pm x_3^2$ $x_2 + x_0, x_0 \pm x_2^2 \pm x_3^2, x_2 + x_0 x_3,$ $x_2 \pm x_0 x_2 + x_0^3 \pm x_0 x_3^2$ $x_0 + x_3, x_0 \pm x_3^2 + \rho_3(x_0^3 + x_0 x_2, x_2),$ $x_3 \pm x_0^2 + x_0 \rho_4(x_0^3 + x_0 x_2, x_2)$ $\pm x_0 + \rho_5(x_0^4 + x_0^2 x_2 + x_0 x_3, x_2, x_3)$

where ρ_i ($i = 1, \dots, 5$) are smooth functions.

PROOF. On the basis of Proposition 5.4. we can reduce the classification problem for the generic images $T^*\rho_K(dF)$ to the classification of mapping diagrams

$$R \xleftarrow{\tilde{F}} K \xrightarrow{\rho} X \xrightarrow{\rho} Y$$

endowed with the so-called strong equivalence (see [2]). In the local coordinates of Proposition 5.4. using the Whitney lowerable vector fields on K we can classify the generic singularities of \tilde{F} (see [2], p.356).

Then, as we see from the definition of the reduced constitutive set \tilde{S} , we can take for F an arbitrary smooth extension of \tilde{F} . Taking the trivial extension of F we obtain the list of Proposition 5.5.

§6. COEXISTENCE OF PHASES, EXTENDED APPROACH

We consider the closed system consisting of n moles of Van der Waals gas divided into k open subsystems in equilibrium (composite system §3). Let $(T^*X, d\theta_X)$ be the phase space of this system (cf. [18]).

$$X \cong \mathbb{R}^{3k} : \left\{ (v_i), (s_i), (n_i) \right\}, \quad (v_i) = (v_1, \dots, v_k), \\ (s_i) = (s_1, \dots, s_k) \text{ ect.}$$

$$T^*X \cong \mathbb{R}^{6k} : \left\{ (v_i), (s_i), (n_i), (\pi_i), (\tau_i), (\tilde{\mu}_i) \right\}$$

$$\theta_X = \sum_{i=1}^k (\pi_i dv_i + \tau_i ds_i + \tilde{\mu}_i dn_i)$$

where $(v_i), (s_i), (n_i)$ etc. are the molar coordinates corresponding to the division into cells (see [9]). The adjoint variables expressed in the standard thermodynamical coordinates are the following (cr. Section 3).

$$\pi_i = -p_i n_i, \quad \tau_i = T_i n_i, \quad \tilde{\mu}_i = \mu_i - p_i v_i + T_i s_i.$$

Let the internal energy $((v_i), (s_i), (n_i)) \rightarrow \tilde{U}((v_i), (s_i), (n_i)) = \sum_{i=1}^k n_i U(v_i, s_i)$ be the generating function for the space of equilibrium states \tilde{L} of the composite system. The configurational domain $K \subset X$ (attainable states) is defined as follows

$$K = \left\{ \left((v_i), (s_i), (n_i) \right) \in X : v_i > 0, s_i > 0, n_i \geq 0, \right. \\ \left. \text{for } i = 1, \dots, k, \sum_{i=1}^k n_i = n > 0 \right\}.$$

We adapt Definition 5.2. in variational form, to obtain all equilibrium states of the reduced system.

Let $(T^*Y, d\theta_Y)$ be the standard control phase space (see Section 4), i.e., $T^*Y: \{V, S, -p, T\}$, $\theta_Y = TdS - pdV$.

HYPOTHESIS 6.1. Let $\rho: X \rightarrow Y$, $\rho((v_i), (s_i), (n_i)) = \left(\sum_{i=1}^k n_i v_i, \sum_{i=1}^k n_i s_i \right)$ be the canonical submersion. Then the space of equilibrium states $W \subset (T^*Y, d\theta_Y)$ for the reduced (deformed) system is represented as the reduced constitutive set $T^*\rho_K(\tilde{L})$, where \tilde{L} is the corresponding, regular constitutive set in $(T^*X, d\theta_X)$. Now we verify this hypothesis in the case of the Van der Waals system (see Section 4). By Definition 5.2. we have:

$(V, S, -p, T) \in T^*\rho_K(\tilde{L}) \subset T^*Y$ if there exists $((v_i), (s_i), (n_i)) \in K$ such that

$$1^\circ \rho((v_i), (s_i), (n_i)) = (V, S)$$

$$2^\circ -p\delta\left(\sum_{i=1}^k n_i v_i\right) + T\delta\left(\sum_{i=1}^k n_i s_i\right) \leq \delta \tilde{U}((v_i), (s_i), (n_i))$$

for all displacements $((\delta v_i), (\delta s_i), (\delta n_i))$ compatible with K .

According to the structure of K we have the two cases:

(K') ; $n_i > 0$ for $i = 1, \dots, k$ (k subsystems)

$$TK' = \left\{ \left((\delta v_i), (\delta s_i), (\delta n_i) \right) ; \sum_{i=1}^k \delta n_i = 0 \right\}$$

taking $\delta n_i \equiv 0$, from 2° we obtain

$$(16) \quad p = - \frac{\partial u}{\partial v_i} (v_i, s_i) , T = \frac{\partial u}{\partial s_i} (v_i, s_i) \quad i = 1, \dots, k .$$

Inserting into 2° , $\delta v_\ell = 0$, $\delta s_m = 0$, for $1 \leq \ell, m \leq k$ and $\delta n_i + \delta n_j = 0$ were $\delta n_r = 0$ if $r \neq i, j$, we obtain

$$(17) \quad -p(v_i - v_j) + T(s_i - s_j) - u(v_i, s_i) + u(v_j, s_j) = 0 .$$

Taking into account the legendre transformation of $u(v, s)$, namely $f_T(v) = u(v, s(v, T)) - Ts(v, T)$, where $\frac{\partial u}{\partial s}(v, s(v, T)) \equiv T$ the equations (16), (17) can be rewritten as follows

$$-p = \frac{\partial f_T}{\partial v_i} (v_i) , \int_{v_i}^{v_j} \left(\frac{\partial f_T}{\partial v} (v) + p \right) dv = 0 .$$

But they are equations obtained in Section 4. for the Van der Waals system. In this case, near the critical point, we have maximally two different solutions with appropriate values of p and T . Let I_1 be a subset of $K = \{1, \dots, k\}$ corresponding to the solution, say (v^1, s^1) , and let $I_2 = K - I_1$ be the subset corresponding to the second solution (v^2, s^2) respectively. Hence we can write: $V = N_1 v^1 + N_2 v^2$, $S = N_1 s^1 + N_2 s^2$, $N_1 = \sum_{i \in I_1} n_i$, $N_2 = \sum_{i \in I_2} n_i$ and .

$$-p = \frac{\partial u}{\partial v} (v^1, s^1) , T = \frac{\partial u}{\partial s} (v^1, s^1)$$

which are equations describing the coexistence of the two phases (see [9]) with the Maxwell convention as a consequence of the approach.

(K'') ; $n_r = 0$ for some $r \in I_1$

Let us suppose that the r -th cell became empty, i.e.

$K'' = \left\{ ((v_i), (s_i), (n_i)) ; v_i > 0, s_i > 0, n_r = 0 \text{ for some } r \in I_1, n_i > 0 \text{ for } i \in K - \{r\} \right\}$. By Definition 5.2. we have

$$(18) \quad -p = \frac{\partial u}{\partial v_i}(v_i, s_i), \quad T = \frac{\partial u}{\partial s_i}(v_i, s_i) \quad \text{for } i \in K - \{r\},$$

$$v = v^1 \sum_{j \in I_1 - \{r\}} n_j + v^2 \sum_{i \in I_2} n_i, \quad s = s^1 \sum_{j \in I_1 - \{r\}} n_j + s^2 \sum_{i \in I_2} n_i$$

and

$$TK|_{K''} = \left\{ ((\delta v_i), (\delta s_i), (\delta n_i)) ; \sum_{i \in K} \delta n_i = 0, \delta n_r \geq 0 \right\}.$$

Let us take

$$\delta n_j = - \sum_{i \in K - \{j\}} \delta n_i$$

for some $j \neq r$. Substituting this formulae to 2° we obtain

$$\sum_{i \in K - \{j\}} (-pv_i + Ts_i + pv_j - Ts_j) \delta n_i \leq \sum_{i \in K - \{j\}} (u(v_i, s_i) - u(v_j, s_j)) \delta n_i.$$

By independence of δn_i we have

$$(19) \quad -p(v_i - v_j) + T(s_i - s_j) = u(v_i, s_i) - u(v_j, s_j), \quad \text{for } i, j \neq r$$

$$(20) \quad -p(v_r - v_j) + T(s_r - s_j) \leq u(v_r, s_r) - u(v_j, s_j), \quad 1 \leq j \leq k$$

It is easy to check that (20) is automatically fulfilled and (18) together with (19) reconstruct the modified Van der Waals variety (see Fig. 3 .).

REMARK 6.2. Considering the conditions 1°, 2° for generic potential function $f_T(v)$ (see [9], [16]) we obtain the triple points (i.e. coexistence of three phases). The presented geometrical approach can be easily extended into more general thermodynamical systems providing quite useful methods for unifying the descriptions of phase transitions in complicated systems (cf.[13]). Moreover one can find easily the universal geometrical meaning for majority of standard procedures in classical theory of phase transitions (see [18], [21], [9]).

Let us adapt our methods to the chemical equilibrium (cf. [9]). Let $(T^*\tilde{X}, d\theta_{\tilde{X}})$ be the phase space of the spatially and chemically (with many ingredients) composite system.

$$\tilde{X} : \left\{ (p_i), (T_i), (n_{ji}) \right\}, T^*\tilde{X} : \left\{ (p_i), (T_i), (n_{ji}) ; (V_i), (-S_i), (\mu_{ji}) \right\}$$

$$\theta_{\tilde{X}} = \sum_{i=1}^k \left(-S_i dT_i + V_i dp_i + \sum_{j=1}^m \mu_{ji} dn_{ji} \right)$$

where "i" numbers the cells and "j" numbers the chemical components of the cells.

For simplicity we assume now that only one phase realizes and only one chemical reaction can appear. So the corresponding phase space for this chemical composite system is as follows

$$(T^*X, d\theta_X) , T^*X : \{p, T, n_j; V, -S, \mu_j\}$$

$$\theta_X = -SdT + Vdp + \sum_{j=1}^m \mu_j dn_j ,$$

where n_j are mole numbers of the chemical components. The chemical reaction is commonly symbolized by equation (see [9])

$$(21) \quad \sum_{i=1}^m v_i B_i = 0 ,$$

where v_i are stoichiometric coefficients.

Equation (21) shows that the changes in mole numbers of all substances taking part in the reaction are completely determined by a single mole number, say n_1 . The course of reaction can, therefore, be described in the form $dn_i = v_i d\hat{A}$, $i = 1, \dots, m$ where \hat{A} is called the progress variable (cf. [9]). $\delta\hat{A}$ is the increment in the time the reaction takes place. Thus the phase space adapted to the presence of chemical reactions can be defined as

$$\left(T^*(X \times R^r) , d\theta_{X \times R^r} \right) ,$$

where r is a number of reactions (here $r = 1$). R^r is the space of so-called progress parameters.

Let $(T^*Y, -SdT + Vdp)$ as before be the standard thermodynamical phase space and $\rho : X \times R \rightarrow Y$, $\rho(p, T, (n_j), \hat{A}) = (p, T)$. Thus the corresponding constitutive set $Q \subset T^*Y$ in the presence of chemical reaction can be written as follows (see Definition 5.2. and Hypothesis 6.1.)

$$(22) \left\{ \begin{array}{l} (p, T, V, -S) \in Q \subset T^*Y \text{ if there exists } (p, T, (n_i), \hat{n}) \in C, \\ \text{such that} \\ V\delta p - S\delta T \leq \delta G(p, T, (n_i), \hat{n}) \\ \text{for all virtual displacements compatible with } TC \cap Z, \end{array} \right.$$

where $C = \{(p, T, (n_i), \hat{n}) : p > 0, T > 0, n_i \geq 0\}$, $Z \subset T(Y \times R)$ is a distribution defined by the reaction

$$Z = \left\{ \left(\delta p, \delta T, (\delta n_i), \delta \hat{n} \right) ; \delta n_i = \nu_i \delta \hat{n}, i = 1, \dots, m \right\}$$

and $G : X \times R \rightarrow R$ is a generating function (free enthalpy [9]) for the space of equilibrium states \tilde{L} in the phase space $(T^*(X \times R), d\theta_{X \times R})$ of the composite system. G does not depend directly on \hat{n} .

Let us suppose (without restriction of generality) that all chemical components are either reactants or products of the considered reaction. Hence we have to take into account the four steps of the variational principle (22).

1°. $(p, T, n_i, \hat{n}) \in C, n_i > 0$.

$$V\delta p - S\delta T \leq \frac{\partial G}{\partial p} \delta p + \frac{\partial G}{\partial T} \delta T + \sum_{i=1}^m \frac{\partial G}{\partial n_i} \delta n_i$$

where $\delta n_i = \nu_i \delta \hat{n}$. So we have:

$$V = \frac{\partial G}{\partial p}, \quad S = -\frac{\partial G}{\partial T}, \quad \sum_{i=1}^m \frac{\partial G}{\partial n_i} \nu_i = 0$$

where the last condition expresses the equilibrium condition (cf. [9])

$$\sum_{i=1}^m \mu_i \nu_i = 0$$

when all reactants and products are present.

2°. not all products are present

Let $n_r = 0$ for some $r \in I_2$ ($\nu_r > 0$), where the subset of indices I_2 corresponds to the products and the subset I_1 corresponds to reactants respectively. Now we have

$V\delta p - S\delta T \leq \frac{\partial G}{\partial p} \delta p + \frac{\partial G}{\partial T} \delta T + \sum_{i=1}^m \frac{\partial G}{\partial n_i} \delta n_i$, where $(\delta p, \delta T, (\delta n_i), \delta \hat{A})$ is such that $\delta n_r \geq 0$ and $\delta \hat{A} \geq 0$. So we obtain

$$V = \frac{\partial G}{\partial p}, \quad S = -\frac{\partial G}{\partial T}$$

$$(23) \quad \left(\sum_{i=1}^m \frac{\partial G}{\partial n_i} \nu_i \right) \delta \hat{A} \geq 0 \quad \rightarrow \quad \sum_{i=1}^m \frac{\partial G}{\partial n_i} \nu_i \geq 0$$

If we introduce the quantity

$$A = - \sum_{i=1}^m \mu_i \nu_i = -\Delta G, \quad ,$$

so-called affinity of the reaction, thus (23) corresponds to the well-known criterion for the possibility of reaction

$$\Delta G \geq 0, \quad A \leq 0 \quad (\text{reaction possible})$$

3°. not all reactants are present.

In this case $n_k = 0$ for some $k \in I_1 (v_k < 0)$. Hence analogously as above we obtain

$$V = \frac{\partial G}{\partial p}, \quad S = -\frac{\partial G}{\partial T}$$

$$\sum_{i=1}^m \frac{\partial G}{\partial n_i} \delta n_i \geq 0, \quad ,$$

where $\delta n_i = v_i \delta \hat{n}$, $\delta n_k \geq 0$ and $\delta \hat{n} \leq 0$ (because of $v_k < 0$).

Thus

$$\Delta G = \sum_{i=1}^m \mu_i v_i < 0, \quad A > 0 \quad (\text{reaction impossible})$$

or

$$\Delta G = 0, \quad A = 0 \quad (\text{chemical equilibrium}) \quad .$$

4°. $n_r = 0$ for some $r \in I_2$ and $n_k = 0$ for some $k \in I_1$.

In this case we do not obtain any additional equilibrium condition, because reaction can not appear. This problem reduces to the thermodynamical equilibrium without chemical reactions.

FINAL REMARK:

Let the volume V of the container be subdivided into cells of volume Δ . It is supposed that Δ is so large that it contains many particles, but so small that the potential is practically constant inside Δ . This imposes the condition that the range of potential must be very long, and that the density must be so high that many particles interact simultaneously. For this system we have the following phase space

$$(T^*X, d\theta_X) \quad T^*X : \left\{ T, V, (n_i), -S, -p, (\mu_i) \right\}$$
$$\theta_X = -SdT - pdV + \sum_i \mu_i dn_i$$

where (n_i) defines the configuration of particles. The free energy for this composite system has a form

$$F(T, V, (n_i)) = \sum_i f(T, V, n_i) + \frac{1}{kT} \sum_{i,j} w_{ij} n_i n_j$$

where $-w_{ij}$ is the attractive potential between cells n_i, n_j . The whole variational analysis of the system is analogous to this one conducted in Section 5, nevertheless the proposed formulation provides the natural geometric approach to the continuous media.

The proposed symplectic approach to thermodynamics gives an adequate language for expressing the geometry of constitutive sets and frequently observed reciprocity relations [23]. Our

concept of deformation of the system generalizes the notion of virtual state (cf. [9]) and provides quite effective quantitative analysis of systems near phase transitions. One of the consequences of this approach is a derivation in the very general phenomenological context, the so-called Maxwell rule [22] which gives a hope that the very peculiar constitutive space of states in mechanics and thermodynamics can be resolved by the canonical symplectic procedures.

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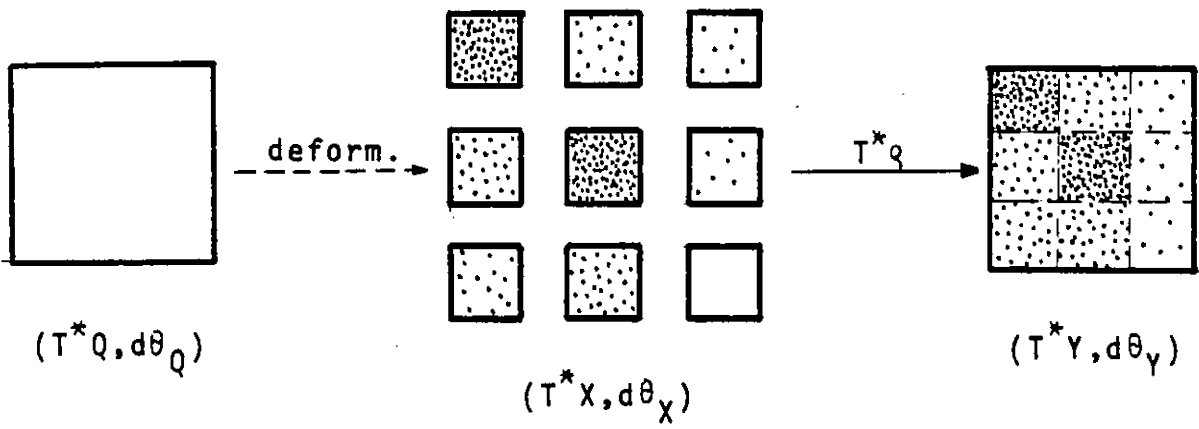


Fig. 1.

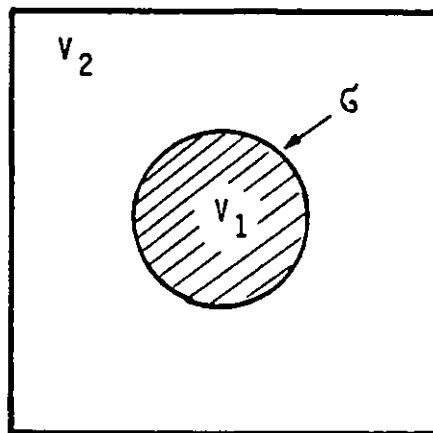


Fig. 2.

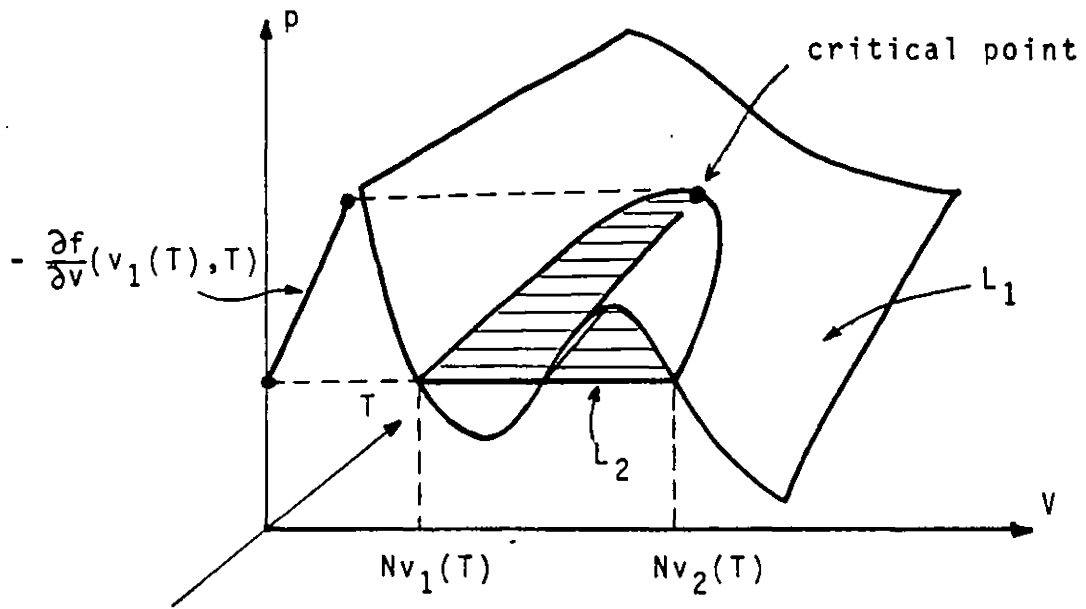


Fig. 3.

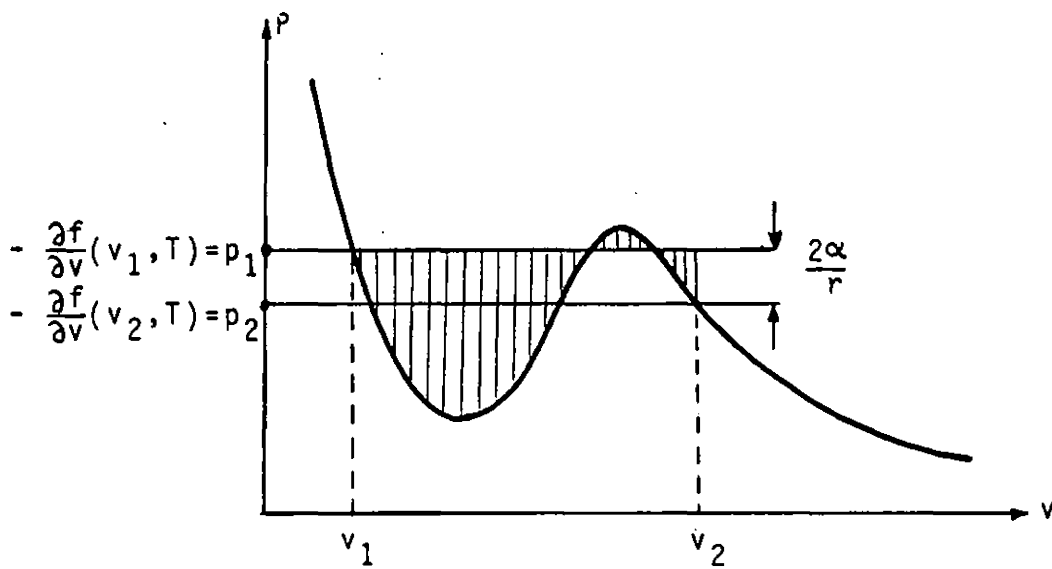


Fig. 4.

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