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SCALING EQUATION OF THERMODYNAMICAL SURFACE OF FLUID. CLOSE VICINITY OF EQUILIBRIUM STATE

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Introduction

In this and other publications which are to follow it´s supposed to set forth a new method of research thermodynamical surface (TS) equilibrium states of one-component fluid, including areas of liquid and gas phases, and also areas of phase transition of the first and second types. A possibility of unified approach to macroscopic description of substance which is characterized in the indicated areas of TS by considerable differencies in microscopic behaviour of the system of particles is secured by thermodynamically universal method of consideration, which is in many parts close to semiphenomenological theory of critical area (CA) [1-3].

As a non-traditional result of the approach being developed in this research one can consider well-based extention of non-classical, scaling dependencies on the description fluid states, remoting from CA and usually approximated by expansion thermodynamical functions of one or two variables into analitical series :

$$f(x) = \sum_{k=0}^{\infty} a_k x^k \quad (a) \qquad f(x, y) = \sum_{k,l=0}^{\infty} a_{kl} x^k y^l \quad (b)$$

Some extending the domain of validity such series is provided, as it´s known, by using the direct Pade approximants $[\ L/M\ ]_f$, in which polynomial exponents are subordinated to the inequality :

$L + M \leq K$ with integer having restrict value.

In case of singularity of the type observed in CA :

$$f(x) \approx Ao(x_{kp} - x)^{-w}\ , \ w \text{ (non integer) } > 0 \qquad (c)$$

Pade technique - approximants must be generalized as it was demonstrated by M. Fisher [4,5], by describing derivative of logarithm of the function $f(x)$: $[L/M]_{d/dx}(\ln f)$ This work propose an alternate method of research of TS particulars basingon the results of catastrophe theory [6,7].

1. It's known that equilibrium thermodynamics (ET) was formulated by Gibbs in locally - differential aspect and based on supposition of fundamental TS existence :

$$E = E\,(N,\ V,\ S) \qquad (1)$$

in each point of which the following differential form on (1) is fulfilled :

$$dE = -PdV + \mu dN + TdS \qquad (2)$$

The empirical principle of macroscopical equivalence employable for N-systems in the volumes of $Vo > Vc$ (Vc-correlational volume of an equilibrium state gives opportunity to introduce the condition of homogeneity of the first degree for the function (1):

$$E = \frac{\partial E}{\partial V}\,V + \frac{\partial E}{\partial N}\,N + \frac{\partial E}{\partial S}\,S \qquad (3)$$

According to (2,3) the following definitions of field variables : $\{bj\} = (-P,\ \mu, T)$ are obtained with the use of initial extensive variables :

$$-P = \partial E/\partial V\ ,\quad \mu = \partial E/\partial N\ ,\quad T = \partial E/\partial S \qquad (4)$$

and also relationship between densities: $\{aj\} = (\varepsilon, \varrho, \sigma)$:

$$\varepsilon = E/V\ ,\quad \varrho = N/V\ ,\quad \sigma = S/V \qquad (5)$$

and field variables is fulfilled :

$$\varepsilon = -P + \varrho\mu + \sigma T \qquad (6)$$

In ET equation (6) gives definition of comlete Legendre transformation of independent variables for reversible changes between local potentials : $\varepsilon\ (\varrho,\ \sigma)$ and $P\ (\mu,\ T)$.

Formally, the indicated potentials could be considered as appropriate solutions of differential equations with partial derivatives of the first order :

$$P(\varrho,\ \sigma;\ \varepsilon;\ \partial\varepsilon/\partial\varrho,\ \partial\varepsilon/\partial\sigma) = 0 \qquad (7)$$

$$P(\mu;\ T;\ P;\ \partial P/\partial\mu,\ \partial P/\partial T) = 0 \qquad (8)$$

Each from these equations is equivalent to the relation ET (6), having form of generalized equation of Clerout [8]. We take a variant of field b_j-representation (8) (a complete symmetrical calculations can be made for density a_j-representation (7)) and formulate a task of constructing integral TS :

$$P = P(\mu, T) \qquad (9)$$

in every point of which similar to (1,2), the following differential form is fulfilled :

$$dP = \varrho d\mu + \sigma dT \qquad (10)$$

The equation (10) gives the condition for the flat elements (points $q_o \in \mathfrak{P}^{n=2}$and tangent to TS (9) at these points of planes $T_{qo}\mathfrak{P}^{n=2}$) :

$$P^* - P_o = \varrho_o(\mu - \mu_o) + \sigma_o(T - T_o) \qquad (11)$$

We shall demonstrate that this determined description of q_o point, used in numerous local abstract geometrical representations of ET [9-12] is to be naturally connected with the existence of infinite potential barrier, restricting possible shifts (fluctuations) δq of the point, depicting of equilibrium state on TS (9), from q_o position.

Beyond from physical reasons which can cause such a shift and, thus, from the meaning implied in "time" - parameter τ the changes of generalized coordinates $\{q_j\}$ are called in this work "thermodynamical (T-) movement". Any element of T-movement is characterized in the close vicinity of q_o by set of differentiated functions, belonging to $\mathfrak{P}$,depending from the parameter "T-time" τ:

$$\mu = \mu(\tau);\ T = T(\tau);\ P = P(\tau);\ \varrho = \varrho(\tau);\ \sigma = \sigma(\tau) \qquad (12)$$

The differential equation (6) with suppositionally known form of function $\varepsilon(\varrho, \sigma)$ and the condition Gibbs-Duhem (10) in general case correspond to system of characteristical equations of T-movement representing (depicting) point q_o:

$$\frac{dP}{d\tau} = \varrho\frac{\partial\mathfrak{P}}{\partial\varrho} + \sigma\frac{\partial\mathfrak{P}}{\partial\sigma} \quad (a) \qquad \frac{d\mu}{d\tau} = \frac{\partial\mathfrak{P}}{\partial\varrho} \quad (b) \qquad \frac{dT}{d\tau} = \frac{\partial\mathfrak{P}}{\partial\sigma} \quad (c)$$

$$\frac{d\varrho}{d\tau} = -\left(\varrho\frac{\partial\mathfrak{P}}{\partial P} + \frac{\partial\mathfrak{P}}{\partial\mu}\right) \quad (d) \qquad \frac{d\sigma}{d\tau} = -\left(\sigma\frac{\partial\mathfrak{P}}{\partial P} + \frac{\partial\mathfrak{P}}{\partial T}\right) \quad (e) \qquad (13)$$

Inserting (6) into (13) and taking into account additional conditions, imposed (7) by formalism of ET :

$$\frac{\partial\mathfrak{P}}{\partial\varrho} = -\mu + \frac{\partial\varepsilon}{\partial\varrho} = 0 \; , \qquad \frac{\partial\mathfrak{P}}{\partial\sigma} = -T + \frac{\partial\varepsilon}{\partial\sigma} = 0 \qquad (14)$$

it's not difficult to check, that the integral surface in determined description is degenerated into immovable point of transformation of variables depending on changes of τ-parameter :

$$\frac{d\mu}{d\tau} = \frac{dT}{d\tau} = \frac{dP}{d\tau} = \frac{d\varrho}{d\tau} = \frac{d\sigma}{d\tau} = 0 \qquad (15)$$

2. For finding out physical meaning of the indicated transformation we shall point out that transition into ET from extensive variables $\{A_j\}$ (1-3) to the intensive variables $\{a_j\}$ (5-8) is done with the reduction of one unit from number of independent variables by selecting one of them (V) as a scale of N-system. The possibility of this is secured by empirical condition (3), according to which thermodynamical properties of the equilibrium fluid in a fixed macroscopic volume V_o with a sufficient accuracy are represented by the properties of fluid in a unit of measurement (scal e) volume V_τ.V_τ - value and the way of imaginary placing V_τ-subsystems into initial macroscopical volume V_o in ET is not specified, following the only requirement of macroscopicity : $V_\tau \geq V_c$. If this requirement is fulfilled the value of V_τ or, what is equivalent, the value of nondimensional relation V_o/V_τ, numerically equal to the value of V_o are considered in ET as irrelevant variables at a selected scale V_τ. In T-limit which is determined by the condition of preserving in case $(V_o, V_\tau) \longrightarrow \infty$ of all three densities (5), fluctuations δq, which are always present in real V_τ-subsystems of finite volumes disappear :

$$q_{V\tau} = q_o + \delta q(V_\tau) \qquad \delta q(V_\tau) \longrightarrow 0 \text{ at } V_\tau \longrightarrow \infty \qquad (16)$$

and the description of (x_i, t) - homogeneous $(\partial/\partial x_i = 0, \; \partial/\partial t = 0)$ limited L-system $(V_\tau \longrightarrow \infty, \; V_o/V_\tau \longrightarrow \infty)$ may be given according (1-6) with the help of extensive variables as well as with the help of intensive variables. In this case because of (6), fields $\{b_j\}$ and densities $\{a_j\}$ of ET, is completely equivalent (7,8) and predominant usage in statistical mechanics coordinated basis of density variables $\{q_i\} = \{\varrho, \varepsilon\}$ is caused in possibility of their microscopical interpretation.

Using the admission (x_j, t) - homogeneity to the finite values of V_τ is a certain idealization of the task of describing N-system of great number of moving and interacting particles. With the reduction of V_τ-values, each from V_τ-subsystems, which can be imagined as a separate one within fixed volume V_o, becomes more and more dependent on (x_i, t) parameters of physical space-time. The mentioned dependence reflects really existing into the small volumes $V_\tau(x_i, t)$ nonhomogeneities $(\partial/\partial x_i \neq 0, \; \partial/\partial t \neq 0)$ in distribution of substance and energy. The enumarated facts are associated with the introduction of a limit value V_c into the theory of fluid $(V_\tau \geq V_c)$, below which thermodynamical description is nonapplicable. Thus, the statistical mechanics does not examine the behaviour of the substance in volumes $V_\tau < V_c$, and definitions of densities in the field theory, being more general than (5) :

$$a_j(x_i, t) = \lim_{\Delta V \to V_c} \Delta A_j/\Delta V = \bar{d}A_j/dV \qquad (17)$$

are based on (not quite satisfactory from mathematical point of view) concept of "macrodifferentials" $\bar{d}$("infinitesimal physically").

From this it immediately follows that in ET as τ-parameter in equation (13, 15) one can use nondimensional value :

$$\tau = V_o/V_\tau \qquad (18)$$

If the equilibrium of fluid is considered in a fixed finite V_o-volume and no formal transition to T-limit ($V_o \to \infty$) is applied for the removal of border effects of interaction of V_o-subsystems with the surrounding then the admission of (x_i, t)-homogeneity at $V_\tau \to \infty$ will correspond to q_o point at value of $\tau = 0$. For the finite volumes V_τ, in which also it's necessary to take into account the exchange of V_τ-subsystems with the surronnding by the substance and the energy a determined definition of coordinates of point q_o is equivalent to supposition about an absent of fluctuations $\delta q(\tau)$ within the whole interval : $\tau \in [0, \tau_c = V_o/V_c]$.

If now we supplement the consideration of $[0, \tau_c]$ - area which is further called "area of a-states" with the admission of possibility of continuous change of scale volume V_τ [3]and, hence, the value of T-time τ(18), then physically the following interpretation of ET within the theory of dynamical system (DS) [13, 16] will not appear as inconsistent. At a determined description of "long time" behaviour of a-states, starting from the moment of $\tau = 0$ and up to the moment $\tau = \tau_c$, on the smooth TS q_o - point corresponds to asymptotically stable state of equilibrium, possessing infinite potential barrier, opposing T-movement.

3. We point out, that local thermodynamical potentials $\varepsilon(\varrho,\sigma)$ and $P(\mu,T)$ are not potentials in a mechanical sense, since their gradients at the point of equilibrium are not equal to zero, but determine "canonically conjugated" with coordinates $\{q_j\}$ "impulse" variables $\{\mathfrak{P}_j\}$ by formula (14) for $\xi(\varrho,\sigma)$ and similarly, by formula :

$$\mathfrak{P}_1 = \varrho = \frac{\partial P}{\partial \mu} = \frac{\partial P}{\partial q_1} \quad (a) \qquad \mathfrak{P}_2 = \sigma = \frac{\partial P}{\partial T} = \frac{\partial P}{\partial q_2} \quad (b) \qquad (19)$$

for $P(\mu,T)$ (9) function. In mechanics a function of mechanical action possesses similar property. In ET this type of function must not depend explicitly on the parameter T-time τ. Taking this into account the equation (10) determines a complete derivative on τ :

$$\frac{dP}{d\tau} = \frac{dW}{d\tau} = \sum_j \frac{\partial W}{\partial q_j} \frac{dq_j}{d\tau} = \sum_j \mathfrak{P}_j \frac{dq_j}{d\tau} \qquad (20)$$

and, simultaneously, gives a particular form of dynamical equation of Hamilton-Jacobi :

$$\frac{\partial W}{\partial \tau} = -H(q_j;\ \mathfrak{P}_j) = -H(\mu,T;\varrho,\sigma) = 0 \qquad (21)$$

Where a new notion is introduced of τ-homogeneous, conserving (and at the same time equal to zero) on the trajectory of T-motion T-hamiltonian ET : $H(q_j;\ \mathfrak{P}_j)$.

It's obvious, that suggested dynamical formalism is completely adequated thermodynamically, but it does not provide a solution of the task of finding explicit form of function (9), since T-hamiltonian $H(q_j;\ \mathfrak{P}_j)$ (21) is also a priori unknown, as well as T-action $W(q_j)$. It's interest, that similar correlation in ET between thermodynamical analogues of W and H as was demonstrated by M. Peterson [11] , with the use of less general than discussed above method, can be found between local potentials ET : $e(v,s) \Leftrightarrow W(q_1, q_2)$ and equation of state (ES) in the form:

$$H(q_1;\mathfrak{P}_1,\mathfrak{P}_2) = H(v;P,T) = 0 \qquad (22)$$

Really, as a scale of N-system, taking into account (3), this approach uses N-number and T-impulses $\mathfrak{P}_j$, are :

$$\mathfrak{P}_1 = -P = \frac{\partial e}{\partial v} = \frac{\partial W}{\partial q_1} \quad (a) \qquad \mathfrak{P}_2 = T = \frac{\partial e}{\partial s} = \frac{\partial W}{\partial q_2} \qquad (23)$$

In comparison with (21) T-hamiltonian (22) has even more specific form, in which one from generalized coordinates $q_2 = s$ is of cyclical type that is not included into the expression for $H(q_j;\ \mathfrak{P}_j)$ explicitly.

It's known in the mechanics that conjugate to this coordinate impulse $\mathfrak{P}_2 = T$ is conserved and the trajectories of T-motion in representation of ET (22-23) should be identified with isotherms.

For them the system of equations (13) is transformed into more simple form :

$$\frac{de}{d\tau} = P\frac{\partial H}{\partial P} + T\frac{\partial H}{\partial T} \quad (a) \qquad \frac{dv}{d\tau} = -\frac{\partial H}{\partial P} \quad (b)$$

$$\frac{ds}{d\tau} = \frac{\partial H}{\partial T} \quad (c) \qquad \frac{dP}{d\tau} = \frac{\partial H}{\partial v} \quad (d) \qquad \frac{dT}{d\tau} = 0 \quad (e) \qquad (24)$$

in which the place of $\mathfrak{P}$-function from (7, 8) is taken by function H (22), not containing explicitly of finding dependence e (v, s) and one from coordinates : s. Hence, the equation (24,b-e) determines system 2n of canonical equations of ET. The possibility of its integration is associated in dynamical theory with the determining of T-hamiltonian $H(q_j; \mathfrak{P}_j)$ form and in ET it's equivalent to finding calorical properties (e, s) on the isoherms using known form of thermal ES (22) and initial data (e_o, s_o).

This traditional thermophysical approach which has been discussed above within the limits of Cauchy task for the system of dynamical equations of Hamilton type with the formal parameter T-time τ may have constructive sense for the investigation of the properties fluid in that case if the selected parameter τ is corresponded to the physically correcting model of T-motion of the representing point from initial position q_o on TS. Dynamical interpetation of equations ET (22-24), developed in [11] does not correspond to this requrrement, according to our opinion. To demonstrate it we shall perform usual for the dynamics transition from τ-homogeneous T-hamiltonian H(22) to the dependent on τ function :

$$H(v;P,T) = -P+P(v,T) = 0 \qquad (25)$$

It is not difficult to observe that by this we exersise the replacement of one from "old" coordinates q_1=v by "new" T-time τ=v at the expense of that the dimentions of configurational Q^{n-1} space and, correspondigly, phase $\mathfrak{P}^{2n-2}$ space of ET are reduced.

Then for the isotherms, according to (24), we can get known in ET equations:

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \qquad \left(\frac{\partial e}{\partial v}\right)_T = -P + \left(\frac{\partial P}{\partial T}\right)_v \qquad (26)$$

which is, of course, not providing any new information about TS properties e(v,s), as compared with ET.

In the theory of Hamilton - Jacobi a form (25) representing special type of "new" T hamiltonian, coinsiding with one of the "old" T impulses :

$$\mathfrak{P}_1 = \mathfrak{P}_1(\tau; \mathfrak{P}_2) \qquad (27)$$

which is not depend on cyclical coordinate : q_2=s. We take notice of the fact that any from great number semiempirical (van-der-Waals type) and empirical (polynomial type) thermal ES in form (22) can be interpreted now as a selection of the model of T-hamiltonian (27).

The purpose of present work consists in the development of a new method of research of fluid properties in various areas of TS using T-dynamical formalism of the task being discussed. Physical basis of the suggested approach is related to the above given interpretation of parameter T time τ (18), determining continual change of the scale of measurement (v_τ) of the fixed V_o volume of N-system being researched.

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