APPLICATION OF THERMODYNAMICS OF SYSTEMS IN A FORCE FIELD TO THE EQUILIBRIUM PROPERTIES OF REAL FLUIDS. BASIC RELATIONS FOR PURE SUBSTANCES

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The real fluid, between the molecules of which intermolecular forces are acting is regarded as an ideal fluid without molecular interaction situated in an external force field. A force potential is assigned to this virtual force field, and it is shown that all the equilibrium properties of real fluids can be expressed in terms of this virtual potential or/and of its derivatives. Equations are given, expressing the common state functions of pure substances as functions of the virtual potential. In addition, it is shown that close relationships do exist between the approach mentioned above and the known fundamental approaches, such as the dynamical and statistical-mechanical one. Therefrom it is evident that the approach proposed here represents an additional alternative for the description of equilibrium properties of fluids which is equivalent to the existing approaches from the formal point of view.

In the course of the last two decades, the basic relations of thermodynamics of the systems being found in a force field[1] have been successfully applied to a number of physico-chemical problems[2-15]. The basic and common idea of all these applications consisted in making use of the macroscopic thermodynamics of systems in a force field for description of volume microelements of real systems. These applications appeared as the most direct ones in the case of phenomena on the phase boundary, where the effect of the adjacent phase on the mass in the interface could be plausibly interpreted as an action of an external force field. This conception comes nearest to the adsorption on solids[2-5,13], where in the case of an inert adsorbent, this external force action remains practically constant.

The approach mentioned above has been essentially conserved even in the case of phenomena on mobile interfaces, such as the surface tension[7-12] or the interfacial tension[14,15], where, of course, it was not further possible to consider the acting force field as constant. To obtain practically usable models, it was necessary to introduce additional assumptions.

The applicability of thermodynamics of systems in a force field is not limited of course only to phase boundaries, as it has been shown in the paper[6], where the state behaviour of real gases has been treated in this way, that means as the behaviour

of a homogeneous phase. Here, the basic idea consisted in influencing a volume microelement of the real gas by the force field of one molecule. The mathematical formulation of this idea has led to an integrodifferential equation, the solution of which by successive approximations has yielded results identical with those obtained by means of statical mechanics. This agreement considerably reinforced the confidence in the plausibility of applications of the macroscopic thermodynamics in a force field to microsystems, and, therefore, even in the applicability of this approach to additional physico-chemical problems. Simultaneously, however, it raised a necessity to investigate more closely the foundations of this approach and its relationship to existing methods. These questions are treated in the present paper, where in contrast to the previous ones[2-15], an application to macrosystems is investigated which may be supposed to be clearer and more illustrative.

Basic Ideas

Let us consider a real fluid consisting of molecules between which intermolecular forces are acting. The resulting thermodynamic behaviour of such an ensemble of molecules is determined both by their thermal motion and force interaction. Let us now attempt to describe this real behaviour in the following way. Let us imagine that the molecules, of which the fluid consists, do not interact (except the transfer of impulse in the point particle collision), however, that they are moving in an external force field to which a virtual potential Φ may be assigned. The value of this potential will be selected in a way that this hypothetical system behaves thermodynamically in the same way as the real system, or specificcally, so that the total thermodynamic potential of the substance is the same in both systems. In accordance with the thermodynamics in a force field, the total potential of the hypothetic ideal fluid will be given by the sum of its chemical potential μ^* and the force potential Φ. Denoting the chemical potential of the real fluid as μ we obtained the basic relation

$$\mu = \mu^* + \Phi , \tag{1}$$

where, of course, the total thermodynamic potentials are to be compared under identical conditions. The one component systems, treated in this paper, are bivariant, and to avoid possible ambiguities, we will compare both systems under the same temperature T and the same molar concentration c. Therefore, the chemical potential of the real fluid will be a function of these two intensive variables $\mu(T, c)$, and we can write for the quantity μ^*

$$\mu^* = \mu^{*0}(T) + RT \ln c , \tag{2}$$

since, according to the characteristics given above, the ideal fluid is an ideal gas. The quantity μ^{*0} in the equation (2) denotes the standard chemical potential of an

ideal gas at unit molar concentration. From the preceding, it follows that the virtual force potential Φ will be likewise a function of temperature and concentration

$$\Phi = \Phi(T, c) . \tag{3}$$

To investigate the relationship between this force potential, which is a macroscopic quantity, and the common thermodynamic description, let us consider the state behaviour first.

State Behaviour

A relation expressing the state behaviour of a fluid in terms of the virtual force potential can be obtained in the following way. Combining the equation (*1*) with the equation (*2*) and by differentiating the relation thus formed with respect to the pressure P, we obtain

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{RT}{c}\left(\frac{\partial c}{\partial P}\right)_T + \left(\frac{\partial \Phi}{\partial P}\right)_T . \tag{4}$$

With regard to the validity of the thermodynamic relationship

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V = \frac{1}{c} , \tag{5}$$

where V denotes the molar volume, it is possible to rewrite the equation (*4*) into the form

$$\left(\frac{\partial P}{\partial c}\right)_T = RT + c\left(\frac{\partial \Phi}{\partial c}\right)_T , \tag{6}$$

since the following equation is valid

$$\left(\frac{\partial \Phi}{\partial P}\right)_T = \left(\frac{\partial \Phi}{\partial c}\right)_T \left(\frac{\partial c}{\partial P}\right)_T . \tag{7}$$

Separating the variables in the equation (*6*) and integrating from zero concentration, *i.e.* from zero pressure, an explicit expression for the pressure in an integrated form is obtained

$$P = cRT + \int_0^c c \left(\frac{\partial \Phi}{\partial c}\right)_T \mathrm{d}c , \tag{8a}$$

or

$$P = cRT + \int_0^{\Phi} c \, d\Phi \,, \tag{8b}$$

eventually

$$P = c(RT + \Phi) - \int_0^c \Phi \, dc \,. \tag{8c}$$

The relation (6) is analogous to the thermodynamic state equation, however, in contrast to that, it enables to express the pressure explicitly in the integrated forms $(8a-c)$. We can, therefore, denote the relations $(8a-c)$, or even the relation (6) as the state equations expressed in terms of the virtual potential Φ. For application purposes, it is convenient to formulate the state equation by means of an expression for the product PV of for the compressibility factor z. From the relations $(8a-c)$, the state equations are thus obtained in the forms

$$PV = RT + \frac{1}{c} \int_0^c c \left(\frac{\partial \Phi}{\partial c}\right)_T dc \,, \tag{9a}$$

$$PV = RT + \frac{1}{c} \int_0^{\Phi} c \, d\Phi \,, \tag{9b}$$

$$PV = RT + \Phi - \frac{1}{c} \int_0^c \Phi \, dc \,, \tag{9c}$$

or

$$z = 1 + \frac{1}{cRT} \int_0^c c \left(\frac{\partial \Phi}{\partial x}\right)_T dc \,, \tag{10a}$$

$$z = 1 + \frac{1}{cRT} \int_0^1 c \, d\Phi \,, \tag{10b}$$

and

$$z = 1 + \frac{\Phi}{RT} - \frac{1}{cRT} \int_0^c \Phi \, dc \,. \tag{10c}$$

From the state behaviour, we can now proceed to the common thermodynamic quantities.

Thermodynamic Quantities of the First Law

Knowing the state behaviour, as expressed by the equations (8), (9), or (10) we can obtain the thermodynamic quantities defined by the first law of thermodynamics in the ways which are common in thermodynamics. To obtain an expression for the molar internal energy U, we start from the thermodynamic state equation in the form

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P, \tag{11}$$

wherefrom after combining with the relation (8), we obtain by rearrangeing and integrating an expression

$$U = U^*(T) + \frac{1}{c}\int_0^c\left[\Phi - T\left(\frac{\partial\Phi}{\partial T}\right)_c\right]dc, \tag{12}$$

where $U^*(T)$ denotes the internal energy of the substance in the state of an ideal gas. It is possible to obtain an expression for the molar enthalpy of the fluid in a similar way

$$H = H^*(T) + \Phi - \frac{1}{c}\int_0^c T\left(\frac{\partial\Phi}{\partial T}\right)_c dc, \tag{13}$$

where the symbol $H^*(T)$ signifies the enthalpy of the substance in the state of an ideal gas, which is — analogously to the quantity $U^*(T)$ — a function of the temperature only. Likewise no difficulties are found in deriving expressions for additional thermodynamic quantities of the first law from definitions. Here, let us show an expression for the molar heat capacity at constant volume

$$C_V = C_V^*(T) - \frac{1}{c}\int_0^c T\left(\frac{\partial^2\Phi}{\partial T^2}\right)_c dc, \tag{14}$$

where the heat capacity of the substance in the state of an ideal gas, $C_V^*(T)$, depends on temperature only, and an expression for the difference of heat capacities at constant pressure, C_p, and at constant volume, C_V,

$$C_P - C_V = \left[R + \left(\frac{\partial\Phi}{\partial T}\right)_c - \frac{1}{c}\int_0^c\left(\frac{\partial\Phi}{\partial T}\right)_c dc\right]^2\left[R + \frac{c}{T}\left(\frac{\partial\Phi}{\partial c}\right)_T\right]^{-1}. \tag{15}$$

Thermodynamic Quantities of the Second Law

In the case of pure substancrs, the molar Gibbs energy equals the chemical potential μ and, therefore, according to the equations (1) and (2) we can write directly

$$G = G^{*0}(T) + RT \ln c + \Phi, \tag{16}$$

where the quantity G^{*0} is of the same significance as the μ in the equation (2). From what preceded, an expression for the molar Helmholtz energy, F, may be easily derived in the form

$$F = F^{*0}(T) + RT \ln c + \frac{1}{c} \int_0^c \Phi \, dc, \tag{17}$$

and an expression of the molar entropy, S, of the substance as well

$$S = S^{*0}(T) - R \ln c - \frac{1}{c} \int_0^c \left(\frac{\partial \Phi}{\partial T}\right)_c dc. \tag{18}$$

The quantities F^{*0} and S^{*0} in the given expressions denote the Helmholtz energy and entropy of the substance in the state of an ideal gas at unit concentration; the both quantities are dependent on the temperature only.

From the additional quantities based on the second law of thermodynamics, let us mention at least the fugacity and the fugacity coefficient. Substituting into the definition equation of fugacity, f,

$$RT \, d \ln f = d\mu(T) \tag{19}$$

for the chemical potential from the combined equations (1) and (2), a relation is obtained

$$d \ln (f/c) = d\phi/RT, \tag{20}$$

from which on integrating within limits from zero to c and on rearranging, an expression follows for the fugacity as a function of the virtual potential Φ

$$f = cRT \exp (\Phi/RT). \tag{21}$$

That is, it can be easily shown that for the lower limit of the ratio of f/c, the following is valid

$$\lim_{c \to 0} (f/c) = RT. \tag{22}$$

An expression for the fugacity coefficient v is obtained on substituting the relation (21) into the definition equation $v = f/P$ and on rearranging in the form

$$v = RT \exp (\Phi/RT) \cdot \left[RT + \Phi - \frac{1}{c} \int_0^c \Phi \, dc \right]^{-1}. \tag{23}$$

Concluding this survey of relations between the thermodynamic quantities and the virtual potential, let us show in addition an inverse relation expressing the potential as an explicit function of thermodynamic quantities. By multiplying mutually both sides of equations $(10c)$ and (23), we obtain on rearranging a simple relation

$$\Phi = RT \ln (zv) \qquad (24)$$

which permits to calculate the virtual potential from the commonly accessible quantities such as the compressibility factor and the fugacity coefficient.

All the equations shown up to now represent quantitative relations between the virtual potential Φ and the quantities of macroscopic thermodynamics. No doubt, it will be likewise interesting to investigate the relationship of the virtual potential to the quantities arising out of the more fundamental approaches, such as the methods based on statistical thermodynamics of on the virial theorem.

Relationship to Statistical Thermodynamics

From the statistical thermodynamics[16], a relation follows between the Helmholtz energy, F, and the partition function of the canonical ensemble, Q, in the form

$$F = -RT \ln Q \qquad (25)$$

and on comparing it with the equation (17), it is possible to express, after rearrangement, the partition function as a function of the virtual potential

$$Q = Q^* \exp \left[-\frac{1}{cRT} \int_0^c \Phi \, dc \right]. \qquad (26)$$

From this equation, where the symbol Q^* denotes the partition function of an ideal gas under the same conditions (c, T), it is possible to obtain easily the inverse dependence of the virtual potential on the partition function in an explicit form

$$\Phi = -RT \left[\ln \frac{Q}{Q^*} + \left(\partial \ln \frac{Q}{Q^*} \middle/ \partial \ln c \right)_T \right]. \qquad (27)$$

Relationship to the Virial Theorem

In accord with the virial theorem[17], the average kinetic energy of an ensemble of molecules is equal to the virial of the forces Ξ, which is defined by the relation

$$\Xi = -\tfrac{1}{2} \cdot \sum_j \overline{(\mathbf{r}_j \cdot \mathbf{F}_j)}. \qquad (28)$$

In this relation, the $\boldsymbol{r}_j$ is the radiusvector of the j-th particle on which a force $\boldsymbol{F}_j$ is acting, and the upper bar denotes the values of the above product averaged with respect to time. Decomposing the total virial of the forces, defined by the equation (28), into the virial of the intermolecular force Ξ_i and into the virial of the external forces Ξ_e, the following relation according to the virial theorem results[17]

$$PV = RT - \tfrac{2}{3}\Xi_i , \tag{29}$$

since the external virial is given by the forces which are exerted on the fluid by the walls of the vessel, so that $\Xi_e = \tfrac{3}{2}PV$. On comparing the equation (29) with the relation $(9c)$, we arrive at an expression for the virial of the intermolecular forces as a function of the virtual potential in the form

$$\Xi_i = -\frac{3}{2}\left[\Phi - \frac{1}{c}\int_0^c \Phi \, \mathrm{d}c \right]. \tag{30}$$

From this equation, it is possible to obtain an inverse function in the explicit form for the virtual potential

$$\Phi = -\frac{2}{3}\left[\Xi_i + \int_0^c \frac{\Xi_i}{c} \, \mathrm{d}c \right]. \tag{31}$$

CONCLUSIONS

The described application of the thermodynamics of systems in a force field to macro-systems leads to the concept of the virtual force potential as a macroscopic quantity depending primarily on the temperature and concentration. By means of this virtual potential, it is possible to express all the quantities used in macroscopic thermodynamics. Here, the relations (8) to (10), (12) to (18), (21) and (23) are given for the basic quantities, which of course do not exhaust all the alternatives, and they are given here rather as an illustration. The virtual potential together with its temperature and concentration dependence represents a complete thermodynamic description of the pure real fluid which is equivalent to the existing thermodynamic methods of description.

In addition, the virtual potential possesses close relationships even to more fundamental molecular approaches, such as the statistical-mechanical or the molecular-dynamical one. The situation is here illustrated by means of simple relationships existing between the partition function and the virial of the forces on one hand, and the virtual potential on the other hand. All these relations may be obtained in an explicit form, even for inverse functional dependences. The relationships between the

virtual potential and the virial of the intermolecular forces are to be considered as especially telling ones. From the formal point of view, the approach proposed here represents an additional alternative. From the molecular point of view, it permits to operate with various degrees of the model rigorousness which can proceed within very broad limits, that is according to the contents of empirism, intuition, or of both these extralogical elements.

In the light of the knowledge mentioned above, the successfulness of the applications of thermodynamics of the systems in a force field made up to now does not appear to be so surprising. The multitude of these applications is of course far from being exhausted by the attempts which have carried out up to now[2-15]. On the contrary, we have to expect a much more frequent occurrence of such applications for which this paper yields a firmer foundation than it was up to the present time.

In conclusion let us mention that the applications of this kind cannot be carried out mechanically, but that they require a highly creative approach, and that their successfulness will be conditioned not only by the adequacy of the used molecular model but also by the usefulness of such a description, especially in comparison with the methods used up to the present.

LIST OF SYMBOLS

c	molar concentration
C	molar heat capacity
f	fugacity
F	molar Helmholtz energy
F_j	force acting on the j-th particle
G	molar Gibbs energy
H	molar enthalpy
P	pressure
r_j	radiusvector of the j-th particle
R	gas constant
S	molar entropy
T	temperature
U	molar internal energy
V	molar volume
z	compressibility factor
μ	chemical potential
ν	fugacity coefficient
$\varXi$	virial of forces
Φ	virtual potential

Superscripts

*	state of ideal gas
o	standard state at unit molar concentration

Subscripts

c	constant concentration
e	external forces
i	intermolecular forces
P	constant pressure
T	constant temperature
V	constant volume

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