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THE MODIFICATION OF THE CHARACTERISTIC FUNCTIONS IN DISPERSE TWO-PHASE ONE-COMPONENT SYSTEMS

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Abstract—The characteristic functions and some state quantities are modified in the presence of phase interface and surface tension. The modification of the free energy, entropy, internal energy, enthalpy, free enthalpy, latent heat, and Clausius–Clapeyron equation will be deduced for both droplets and vapour bubbles of uniform and nonuniform temperatures and size distribution.

NOMENCLATURE

A,	area of phase interface;
C,	constant;
E,	internal energy;
e,	specific internal energy;
F,	free energy;
f,	specific free energy;
G,	free enthalpy;
g,	specific free enthalpy;
H,	enthalpy;
h,	specific enthalpy;
M,	mass;
P,	pressure;
P_s,	saturation pressure;
ΔP,	pressure difference;
R,	radius of disperse particle;
r,	latent heat of vaporization;
S,	entropy;
s,	specific entropy;
T,	temperature;
V,	volume;
v,	specific volume;
z,	function in general;
ρ,	mass density;
σ,	surface tension;
$'$,	refers to liquid phase;
$''$,	refers to vapour phase;
$*$,	refers to disperse state.

THE PRECISE knowledge of the characteristic functions and state quantities plays an important role when describing some thermodynamic relations of the heat- and mass-transfer processes.

According to the theorem of thermodynamics about the surface tension, the characteristic functions and some state quantities of the two-phase systems are different from the algebraic sum of them, corresponding to the separate phases without interface, other circumstances being equal, i.e. their total mass, temperature, and pressure are identical. Therefore, to the precise description of the two-phase systems the additional effects of the surface tension are also to be considered. Their neglect is permissible only in case the undermentioned simplifying assumptions are valid;

—the mass of the interfacial boundary layer is very small in comparison with the total mass of the system;

—the surface tension produces no superpressure within one of the phases, in other words, the curvature of the interface is slight, practically nil.

While investigating the two-phase systems arises the question, to which phase are belonging the variations caused by the surface tension. In case one of the phases is dispersed, it can clearly be seen that the state of this phase is affected predominantly by the surface tension, consequently, these variations may be attached to the disperse phase, while the coherent phase suffers practically no change [1].

Based on this assumption, concerning the characteristic functions it will be attempted to reduce the investigation of the two-phase one-component systems to that of the disperse phase, as seen in the sequel. This treatment can make easier passing over to the systems of two or more components.

The well-known interrelations of the characteristic functions in general are defined as follows:

$$E = F+TS,$$
$$H = E+PV,$$
$$G = F+PV.$$

In case these characteristic functions relate to a single disperse particle surrounded by the coherent phase of the same chemical composition, i.e. to a droplet within vapour bulk, or a bubble within liquid bulk, let us introduce the notation:

$$E_* = F_* + TS_*, \tag{1}$$

$$H_* = E_* + P_* V, \tag{2}$$

$$G_* = F_* + P_* V. \tag{3}$$

If the free energy F belongs to a certain part of the medium without interface, in the presence of the interface the same mass has an increased free energy

$$F_* = F + \sigma A, \tag{4}$$

as shown by Grigull, Bach and Straub [2–4], as well as, by Novikov and Voskresenskiy [5].

The entropy can be deduced from the free energy [6, 7], in this case it is defined by

$$S = -\frac{\partial F}{\partial T},$$

and this definition, by means of the equation (4), results in

$$S_* = S - \frac{\mathrm{d}\sigma}{\mathrm{d}T} A \tag{5}$$

for the entropy modified in the presence of phase interface, as proved by Keenan [8], Novikov and Voskresenskiy [5].

Having replaced the equations (4) and (5) into the definition (1), for the internal energy of the surrounded particle belonging to the disperse phase

$$E_* = E + \left(\sigma - T\frac{\mathrm{d}\sigma}{\mathrm{d}T}\right) A \tag{6}$$

is yielded, as deduced by Keenan [8], Grigull, Bach and Straub [2–4], as well as, by Novikov and Voskresenskiy [5].

It is known that the surrounded particle of the two-phase system always has a superpressure (ΔP) in comparison with the environmental pressure. However, the pressure within the surrounded particle is different not only from the environmental pressure, but also from the saturation pressure (by ΔP_*) corresponding to its own temperature [9].

Under the circumstances, the definition of the enthalpy (2) becomes

$$H_* = H + \left(\sigma - T\frac{\mathrm{d}\sigma}{\mathrm{d}T}\right) A - \Delta P_* V, \tag{7}$$

and the free enthalpy (3) turns into

$$G_* = G + \sigma A - \Delta P_* V, \tag{8}$$

in agreement with the definition of the work required for creating the bubble surface, as explained by Volmer [10] and Tong [11].

When investigating the droplets and bubbles, as a rule, they are assumed spherical ones. According to Laplace's theorem, the capillary superpressure within the spherical particle of disperse phase is given by

$$\Delta P = \frac{2\sigma}{R}. \tag{9}$$

This formula was transformed by Kelvin, considering that the vapour pressure deviates from the saturation pressure by

$$\Delta P'' = P_s - P'' = \mp \frac{2\sigma}{R} \cdot \frac{\rho''}{\rho' - \rho''}, \tag{10}$$

where the upper sign (−) relates to the droplet, and the lower one (+) to the bubble [9].

This means that the difference between saturation pressure P_s and bubble pressure P_*'' is immediately given by the equation (10), while for determining the difference between saturation pressure P_s and droplet pressure P_*' the equation (10) should be completed by the pressure difference between phases ΔP (9). Based on this assumption, the deviation between the pressure within disperse particle of both kinds and the saturation pressure can be defined by

$$\Delta P_* = \mp \frac{2\sigma}{R} \cdot \frac{\rho}{\rho' - \rho''}, \tag{11}$$

where the signs are to be used as above, and the density ρ in numerator always belongs to the disperse phase.

As can be seen from the equations (9)–(11), in case of droplets the pressures in both phases exceed the saturation pressure, and in case of bubbles the pressures in both phases deviate to the contrary. In other words, on condition that a system was in thermal equilibrium, both of its phases would be either subcooled (droplets within vapour bulk), or superheated (bubbles within liquid bulk), according to the usual terminology.

The characteristic functions per unit mass of disperse phase in specific form can be obtained from the equations (4)–(8), replacing the spherical surface and volume, as well as, the pressure difference (11), furthermore, dividing by the mass of a single droplet or bubble, respectively. Provided that the system is of monodisperse character, i.e. the temperature and size distribution in disperse phase is uniform, all these operations result in the following functions which are to be substituted corresponding to saturation state:

$$f_* = f + \frac{3}{R\rho}\sigma, \tag{12}$$

$$s_* = s - \frac{3}{R\rho}\cdot\frac{\mathrm{d}\sigma}{\mathrm{d}T}, \tag{13}$$

$$e_* = e + \frac{3}{R\rho}\left(\sigma - T\frac{\mathrm{d}\sigma}{\mathrm{d}T}\right), \tag{14}$$

$$h_* = h + \frac{3}{R\rho}\left[\sigma\left(1 \pm \frac{2}{3}\cdot\frac{\rho}{\rho' - \rho''}\right) - T\frac{\mathrm{d}\sigma}{\mathrm{d}T}\right], \tag{15}$$

$$g_* = g + \frac{3}{R\rho}\sigma\left(1 \pm \frac{2}{3}\cdot\frac{\rho}{\rho' - \rho''}\right). \tag{16}$$

In the equations (15) and (16) the upper sign (+) relates to the droplet, and the lower one (−) to the bubble.

The general formulation of latent heat

$$r = h'' - h'$$

leaves out of consideration the effect of the surface tension and capillary superpressure. When taking into account also this effect, there are two variants depending on the nature of the two-phase system.

If droplets are dispersed in vapour bulk, with uniform temperature and size distribution, the latent heat per unit mass of liquid phase can be defined by

$$r'_* = h'' - h'_*.$$

In case bubbles of uniform temperature and size distribution take place in a liquid bulk, the latent heat per unit mass of vapour phase can be determined by

$$r''_* = h''_* - h'.$$

Both kinds of the capillary latent heat can be described by means of the common formula

$$r_* = r \mp \frac{3}{R\rho}\left[\sigma\left(1 \pm \frac{2}{3}\cdot\frac{\rho}{\rho' - \rho''}\right) - T\frac{\mathrm{d}\sigma}{\mathrm{d}T}\right], \tag{17}$$

in which the upper signs relate to droplets, while the lower ones to bubbles.

As can be seen, the two kinds of the capillary latent heat are different from the usual one, viz. according to

$$r'_* < r < r''_*,$$

on condition that temperatures and radii are equal. In other words, less heat is required to the evaporation of the liquid phase in case it forms droplets, on the one hand, and during the condensation of the vapour phase forming bubbles more energy will be released than the usual latent heat, on the other hand.

The modification of the characteristic functions is accompanied also by the variation of the Clausius–Clapeyron equation

$$\frac{\mathrm{d}P_s}{\mathrm{d}T} = \frac{s'' - s'}{v'' - v'},$$

what can be determined considering that the pressure of disperse particle is different from the saturation pressure. Thus the Clausius–Clapeyron equation either turns into

$$\left.\begin{aligned} \frac{\partial P'_*}{\partial T} &= \frac{\mathrm{d}P_s}{\mathrm{d}T} + \frac{2\sigma}{R}\cdot\frac{v''}{v'' - v'} \\ &\qquad \times\left(\frac{\mathrm{d}}{\mathrm{d}T}\ln\sigma + \frac{v'}{v'' - v'}\cdot\frac{\mathrm{d}}{\mathrm{d}T}\ln\frac{v'}{v''}\right) \\ \frac{\partial P'_*}{\partial R} &= -\frac{2\sigma}{R^2}\cdot\frac{v''}{v'' - v'} \end{aligned}\right\} \tag{18}$$

for droplets within vapour bulk, or it becomes

$$\left.\begin{aligned} \frac{\partial P''_*}{\partial T} &= \frac{\mathrm{d}P_s}{\mathrm{d}T} - \frac{2\sigma}{R}\cdot\frac{v'}{v'' - v'} \\ &\qquad \times\left(\frac{\mathrm{d}}{\mathrm{d}T}\ln\sigma - \frac{v''}{v'' - v'}\cdot\frac{\mathrm{d}}{\mathrm{d}T}\ln\frac{v''}{v'}\right) \\ \frac{\partial P''_*}{\partial R} &= \frac{2\sigma}{R^2}\cdot\frac{v'}{v'' - v'} \end{aligned}\right\} \tag{19}$$

for bubbles within liquid bulk, where in both cases all the physical variables are to be substituted corresponding to saturation state.

In case the system is of polydisperse character, in other words, if the temperature and size distribution of disperse phase is nonuniform, then an average is to be determined. In this regard there are two different alternatives depending on the nature of distribution. The distribution function may have either discreet or continuous character.

On condition that the disperse phase is composed of discreet groups, in each of them the single spherical particles have temperature T_i and radius R_j, and the mass M_{ij} represents the total mass of these groups, then the average per unit mass of disperse phase can be determined by

$$\bar{z}_* = \frac{\sum_j \sum_i z_*(T_i, R_j) M_{ij}}{\sum_j \sum_i M_{ij}}, \tag{20}$$

in which formula the notation z_* is to be substituted corresponding to

$$z_* = f_*, s_*, e_*, h_*, g_*, r_*$$

from the equations (12)–(17), in turn.

Similarly, in case the disperse phase contains spherical particles of continuous temperature and size distribution, the formula

$$\tilde{z}_* = \frac{\iint z_*(T,R) M \,\mathrm{d}T\,\mathrm{d}R}{\iint M \,\mathrm{d}T\,\mathrm{d}R} \tag{21}$$

yields the average of the above-mentioned functions per unit mass of disperse phase.

Till now we dealt with the characteristic functions concerning the disperse phase, independent of its state of aggregation (droplet or bubble), but, of course, the corresponding physical quantities of the coherent phase are also to be considered, i.e. a weighted average of both the phases should be determined when describing the entire two-phase system.

The surface tension is often assumed as a temperature function what is exact merely in case of a horizontal plain surface. When investigating the droplets and bubbles, they are regarded as spherical ones, and the effect of the curvature can be taken into consideration, using instead of the usual surface tension the formula

$$\sigma_* = \frac{R}{R+2C}\sigma, \tag{22}$$

where C is an empiric constant, which amounts to $10^{-10}-10^{-9}m$, as can be seen in certain sources [8, 12]. From the equation (22) by differentiation

$$\frac{\partial \sigma_*}{\partial T} = \frac{R}{R+2C}\frac{\mathrm{d}\sigma}{\mathrm{d}T} \tag{23}$$

is yielded. Applying these functions, the equations (4)-(19) do keep their forms deduced above, apart from the slight variation that

$$R_* = R+2C \tag{24}$$

should be substituted for the radius R in them.

In case of extremely small sizes also this effect can be considered, if wanted.

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MODIFICATION DES FONCTIONS CARACTERISTIQUES DANS LES SYSTEMES BIPHASIQUES A UN SEUL COMPOSANT

Résumé—Les fonctions caractéristiques et quelques grandeurs d'état sont modifiées en présence de l'interface et de la tension interfaciale. La modification de l'énergie libre, de l'entropie, de l'énergie interne, de l'enthalpie, de l'enthalpie libre, de la chaleur latente et de l'équation de Clausius–Clapeyron est déterminée pour des gouttes et des bulles de vapeur, à température uniforme ou non et avec une distribution de dimension.

DIE MODIFIKATION DER CHARAKTERISTISCHEN FUNKTIONEN IN DISPERSEN ZWEIPHASEN-EINKOMPONENTEN-SYSTEMEN

Zusammenfassung—Die charakteristischen Funktionen und einige Zustandsfunktionen werden unter Berücksichtigung von Phasengrenzflächen und Oberflächenspannungen modifiziert. Die Modifikation der Funktionen für die freie Energie, Entropie, innere Energie, Enthalpie, freie Enthalpie, latente Wärme sowie der Gleichung von Clausius–Clapeyron werden für Tropfen und Dampfblasen von gleichmäßiger und ungleichmäßiger Temperatur- und Größenverteilung abgeleitet.

МОДИФИКАЦИЯ ХАРАКТЕРИСТИЧЕСКИХ ФУНКЦИЙ ДЛЯ ДИСПЕРСНЫХ ДВУХФАЗНЫХ ОДНОКОМПОНЕНТНЫХ СИСТЕМ

Аннотация — Модифицированы характеристические функции и некоторые величины в уравнении состояния при наличии межфазовой поверхности раздела и поверхностного натяжения. Как для капель, так и для пузырьков пара при равномерном распределении и неравномерном распределении их по температуре и размерам получена модифицированная форма свободной энергии, энтропии, внутренней энергии, энтальпии, свободной энтальпии, скрытой теплоты и уравнения Клазиуса–Клайперона.