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THE CHARACTERISTIC FUNCTIONS OF MULTIPHASE FLUID SYSTEMS AND THE THERMODYNAMIC INTERPRETATION OF VAPOUR BUBBLE COLLAPSE

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Abstract—The effects of phase interface and surface tension in multiphase fluid systems are investigated. The modification of the entropy, free energy, internal energy, enthalpy, free enthalpy, and their differentials are deduced for both droplet and vapour bubbles of uniform and nonuniform temperature and size distribution. The investigation yields also the latent heat, the Clausius–Clapeyron equation, and the polytropic exponent, adapted for disperse state. The relationships deduced for one-component systems are generalized for two- and more-component systems. It is presented that in the course of bubble size reduction both the vapour temperature and pressure arise much over the critical values taken in the usual sense, since the saturation state, the coexistence curve, and the critical state are significantly modified because of the bubble size in submicroscopic order of magnitude. Also the interdependence of bubble annihilation and cavitation damage is explained.

NOMENCLATURE

A,	area of phase interface;
c_p,	isobaric specific heat;
c_v,	isochoric specific heat;
F,	free energy;
f,	specific free energy;
G,	free enthalpy;
g,	specific free enthalpy;
H,	enthalpy;
h,	specific enthalpy;
M,	mass;
m,	exponent of deviation from saturation state;
n,	polytropic exponent;
p,	pressure;
p_s,	saturation pressure;
Δp,	pressure difference;
R,	radius of disperse particles;
r,	latent heat of vaporization;
S,	entropy;
s,	specific entropy;
T,	temperature;
U,	internal energy;
u,	specific internal energy;
V,	volume;
v,	specific volume;
z,	function in general.

Greek symbols

δ,	quantity due to intermolecular forces;
κ,	isoentropic exponent;
σ,	surface tension.

Superscripts

$'$,	refers to liquid phase;
$''$,	refers to vapour phase;
$*$,	refers to disperse state.

INTRODUCTION

The description of the thermodynamic processes within disperse fluid systems needs the knowledge of the instantaneous states of the phases. The characteristic functions are able to describe not only the steady state of equilibrium systems, but also the instantaneous state of non-equilibrium systems, as well as the local states of their single homogeneous parts. It is the purpose of this article to give a brief theoretical study of the way in which the superficial thermodynamic functions are effected by surface tension in multiphase fluid systems.

According to the theorem on surface tension, the characteristic functions and some state quantities of multiphase systems are different from the simple 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, independent of the chemical composition of the phases. Therefore, at the precise description of multiphase systems also the additional effects of surface tension are to be considered. The neglect of surface tension effects is permissible only in the case of a horizontal plain phase interface, when the surface tension produces no superpressure within one of the phases, or the curvature of the interface is minute, and the mass of the interfacial boundary layer is slight in comparison with the total mass of the system.

When investigating a multiphase system it is necessary to decide to which phase to attribute the consequences of the superficial effects. It can clearly be seen that mainly the state of the dispersed phase is affected in such a case. Thus the consequences of the state variation may be predominantly attached to the disperse phase, while the coherent bulk phase suffers practically no change [1]. The natural choice is the disperse phase, therefore this convention will be adopted here.

The investigation will be carried out on this basis, and it is intended to consider the behaviour of disperse particles in one-component multiphase fluid systems, then the situation will be considered when the disperse phase consists of two or more components, chemically non reacting.

The fundamental equations of thermodynamics which represent the interrelations among the characteristic functions are defined in general by

$$U = F + TS,$$
$$H = U + pV,$$
$$G = F + pV.$$

In case these characteristic functions refer to a single disperse particle surrounded by the coherent phase (i.e. to a droplet in vapour atmosphere or a bubble within liquid bulk), let us introduce the notation

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

$$H_* = U_* + p_* V, \tag{2}$$

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

If F is the free energy of a certain element of fluid of the same mass as a droplet or bubble but without phase interface, then in the presence of phase interface but other conditions being equal the free energy of this element of fluid turns to

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

where A is the area of the interface surrounding the disperse particle and σ_* the surface tension [1–3].

The entropy is given [3, 4] by

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

a result which may be combined with the equation (4) to give

$$S_* = S - A\frac{\partial \sigma_*}{\partial T}, \tag{5}$$

where S_* is the entropy modified by the presence of phase interface [1, 2, 5].

On substituting the equations (4) and (5) into (1) the internal energy of a single particle belonging to the disperse phase is found to be given [1, 2, 5] by

$$U_* = U + A\left(\sigma_* - T\frac{\partial \sigma_*}{\partial T}\right). \tag{6}$$

It is known that the pressure of surrounded liquid and vapour particles always is higher by Δp than that of the ambient phase. However, the pressure in surrounded particles is different not only from the external pressure, but also from the saturation pressure corresponding to its own temperature, viz. by Δp_*, what will be determined in the sequel.

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

$$H_* = H + A\left(\sigma_* - T\frac{\partial \sigma_*}{\partial T}\right) - \Delta p_* V, \tag{7}$$

and that of the free enthalpy (3) turns to

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

as it was deduced earlier [6] in keeping with the definition of the work required for creating a bubble surface [7, 8].

The surface tension is mostly assumed as a temperature function only, what is exact merely in the case of a horizontal plain interface.

When investigating droplets and bubbles of size small enough, they are assumed spherical ones. At the present stage of theory the effect of size on surface tension is usually taken into consideration by the approximation

$$\sigma_* = \frac{R}{R + 2\delta}\sigma, \tag{9}$$

where δ is a quantity which expresses the effects of intermolecular forces and can be treated nearly constant estimated at 10^{-10}–10^{-9} M, until we get to quite small particle sizes [5, 9, 10]. In the case of very minute radii the accuracy of the approximative expression (9) is not satisfactory [9, 11].

A thermodynamic investigation resulted in the equation

$$\partial\sigma_*/\partial R = \frac{2\delta[1 + (\delta/R) + (\delta^2/3R^2)]}{R + 2\delta[1 + (\delta/R) + (\delta^2/3R^2)]}\cdot\frac{\sigma_*}{R} \tag{10}$$

for the interdependence of the variables in question, where the quantity δ, too, cannot be treated as a constant. Also the possibility should be assumed that the quantity δ might ultimately change sign and thus lead to a minimum of surface tension on going to smaller and smaller radii [12]. Such a behaviour of the surface tension becomes important in connection with the cavitation damage as it will be treated later.

Returning to the above-mentioned pressure differences, according to Laplace's theorem the capillary superpressure within a spherical particle of dispersed state in comparison with the ambient pressure is given by

$$\Delta p = \frac{2\sigma_*}{R}. \tag{11}$$

Moreover, with reference to Kelvin's explanation it is often stated that the vapour pressure is given by

$$p'' = p_s \pm \frac{2\sigma}{R}\cdot\frac{v'}{v'' - v'}, \tag{12}$$

where the upper sign (+) relates to the droplet, and the lower one (−) to the bubble [2, 13, 14, 15]. This expression has been obtained from Taylor's explanation of

$$p'' = p_s \exp\left(\frac{2\sigma_*}{p_s R}\cdot\frac{v'}{v'' - v'}\right). \tag{13}$$

In this equation the surface tension, nevertheless, should be treated corresponding to the foregoing, and the radius is either positive or negative in sign, depending upon the state of aggregation as used above [2, 5, 15, 16].

This means that the bubble pressure is immediately given by the equation (13), but in order to define the droplet pressure this equation should be completed by the pressure difference between phases Δp (11). Consequently, the pressure in a single droplet or bubble can be defined by

$$p_* = p_s \exp\left(\frac{2\sigma_*}{p_s R}\cdot\frac{v'}{v''-v'}\right) + \frac{(1\pm1)\sigma_*}{R}, \qquad (14)$$

and introducing the notation

$$m = \frac{2\sigma_*}{p_s R}\cdot\frac{v'}{v''-v'}, \qquad (15)$$

we obtain

$$p_* = p_s \exp m + \frac{(1\pm1)\sigma_*}{R}, \qquad (16)$$

where the upper sign (+) relates to the droplet, and the lower one (−) to the bubble, consequently, in the latter case the last term on the RHS disappears. The exponent m may be either positive (droplet) or negative (bubble) in sign [15, 16].

On the basis of the equation (16) the difference between saturation pressure and droplet or bubble pressure is given by

$$\Delta p_* = p_s - p_* = p_s(1-\exp m) - \frac{(1\pm1)\sigma_*}{R}, \qquad (17)$$

where the note made above on signs continues to hold.

It follows from the equations (13)–(16) that when droplets are dispersed in a one-component system, the pressures in all the phases exceed the saturation pressure, but if bubbles are dispersed in such a system, the pressures in all the phases deviate to the contrary. In other words, supposing that a multiphase fluid system could be in thermal equilibrium, according to the usual terminology, all the phases would be either subcooled (droplets in vapour atmosphere), or superheated (bubbles within a liquid bulk).

As a matter of fact, the equations (13)–(16) rather mean that not only the characteristic functions, but also the *notion of saturation state itself is modified* under the circumstances. Namely, according to the usual definition of saturation state, the saturation pressure depends exclusively upon temperature. Nevertheless, this statement is valid not in general, merely in the special case $R = \infty$, failing which the saturation state is determined not only by temperature, but also by surface tension and particle size. The instantaneous *saturation state* of a droplet or vapour bubble undoubtedly can be identified by the fact that an infinitesimal *heat transfer* is inseparably accompanied by *phase change*.

The characteristic functions per unit mass of the disperse phase in specific form can be obtained as follows.

Provided that the system is of monodisperse character, i.e. the temperature and size distribution in the disperse phase is uniform, taking the equations (4)–(8), substituting the spherical surface area and volume as well as the pressure difference (17), then dividing through by the mass of a single droplet or bubble, respectively, all these operations result in the functions

$$s_* = s - \frac{3v\,\partial\sigma_*/\partial T}{R}, \qquad (18)$$

$$f_* = f + \frac{3v\sigma_*}{R}, \qquad (19)$$

$$u_* = u + \frac{3v(\sigma_* - T\,\partial\sigma_*/\partial T)}{R}, \qquad (20)$$

$$h_* = h - v\left(p_s(1-\exp m) - \frac{(4\pm1)\sigma_* - 3T\,\partial\sigma_*/\partial T}{R}\right), \qquad (21)$$

$$g_* = g - v\left(p_s(1-\exp m) - \frac{(4\pm1)\sigma_*}{R}\right), \qquad (22)$$

where the upper signs (+) relate to droplets, and the lower ones (−) to bubbles, moreover, the exponent m has the same sign as in the equations (15) and (16).

Having established the enthalpy also the latent heat modified by surface tension can be defined.

In the usual expression of the latent heat

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

the effects of the surface tension and capillary superpressure are disregarded. When taking into account also these effects, there are two variants depending on the nature of the multiphase system.

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

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

If bubbles of uniform temperature and size distribution take place in a liquid bulk, the latent heat per unit mass of the vapour phase is given by

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

On the basis of these relationships both kinds of the capillary latent heat can be described by

$$r_* = r \pm v\left(p_s(1-\exp m) - \frac{(4\pm1)\sigma_* - 3T\,\partial\sigma_*/\partial T}{R}\right), \qquad (23)$$

in which the upper signs (+) relate to droplets in vapour atmosphere, while the lower ones (−) to bubbles within a liquid bulk.

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

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

on condition that temperature and particle size in the disperse phase are equal. This means that in comparison with the usual latent heat less energy is required for the evaporation of the liquid phase if it forms droplets, and, on the other hand, more energy is released during the condensation of the vapour phase if it consists of bubbles.

Based on the foregoing, an opportunity offers itself to define the differentials of the characteristic functions adapted for disperse particles.

The differentials of the fundamental equations (1)–(3) are given by

$$dU_* = dF_* + d(TS_*),$$
$$dH_* = dU_* + d(p_* V),$$
$$dG_* = dF_* + d(p_* V),$$

consequently, by means of the Gibbs–Duhem relation

$$S_* \, dT - V \, dp_* + M \, dg_* = 0, \qquad (24)$$

the differentials of the potential functions can be defined by

$$dF_* = -p_* \, dV - S_* \, dT + g_* \, dM, \qquad (25)$$
$$dU_* = T \, dS_* - p_* \, dV + g_* \, dM, \qquad (26)$$
$$dH_* = T \, dS_* + V \, dp_* + g_* \, dM, \qquad (27)$$
$$dG_* = V \, dp_* - S_* \, dT + g_* \, dM, \qquad (28)$$

and in specific form, when the Gibbs–Duhem relation becomes

$$s_* \, dT - v \, dp_* + dg_* = 0, \qquad (29)$$

the differentials of the potential functions per unit mass of the disperse phase can be described by

$$df_* = -p_* \, dv - s_* \, dT, \qquad (30)$$
$$du_* = T \, ds_* - p_* \, dv, \qquad (31)$$
$$dh_* = T \, ds_* + v \, dp_*, \qquad (32)$$
$$dg_* = v \, dp_* - s_* \, dT. \qquad (33)$$

As can be seen, these equations are different from the usual ones only to such an extent that they contain s_*, ds_*, p_*, dp_*, instead of s, ds, p, dp. The entropy s_* and pressure p_* adapted for disperse state are already available, consequently, their differentials can be determined.

The partial differentiation of entropy s_* (18) and pressure p_* (16), viz. with respect to temperature T and radius R, results in

$$\frac{\partial s_*}{\partial T} = \frac{ds}{dT} - \frac{3v}{R}\left(\frac{\partial \sigma_*}{\partial T} \cdot \frac{d}{dT} \ln v + \frac{\partial^2 \sigma_*}{\partial T^2}\right), \qquad (34)$$

$$\frac{\partial s_*}{\partial R} = \frac{3v}{R}\left(\frac{1}{R} \cdot \frac{\partial \sigma_*}{\partial T} - \frac{\partial^2 \sigma_*}{\partial T \, \partial R}\right), \qquad (35)$$

$$\frac{\partial p_*}{\partial T} = \left(\frac{dp_s}{dT} + p_s \frac{\partial m}{\partial T}\right) \exp m + \frac{1 \pm 1}{R} \cdot \frac{\partial \sigma_*}{\partial T}, \qquad (36)$$

$$\frac{\partial p_*}{\partial R} = p_s \frac{\partial m}{\partial R} \exp m + (1 \pm 1) \frac{\partial}{\partial R} \frac{\sigma_*}{R}, \qquad (37)$$

where the double signs are to be used as above.

Under the circumstances, the entropy differential is determined by

$$ds_* = ds - \frac{3v}{R}\left(\frac{\partial \sigma_*}{\partial T} \, d \ln \frac{v}{R} + \right.$$
$$\left. + \frac{\partial^2 \sigma_*}{\partial T^2} \, dT + \frac{\partial^2 \sigma_*}{\partial T \, \partial R} \, dR\right), \qquad (38)$$

while the differential of the pressure within disperse particles can be defined by

$$dp_* = (dp_s + p_s \, dm) \exp m + (1 \pm 1) \, d \frac{\sigma_*}{R}, \qquad (39)$$

what can be regarded as the analogue of Clausius–Clapeyron equation

$$dp_s = \frac{s'' - s'}{v'' - v'} \, dT,$$

adapted for disperse state, in accordance with the fact that the pressure p_* depends not only on temperature.

Having established the differentials an opportunity offers itself to determine the polytropic exponent n_* adapted for disperse state.

As a matter of fact the isoentropic exponent denotes the quotient of the isobaric and the isochoric specific heat, but the two kinds of specific heat are the differential quotients of the enthalpy and the internal energy with respect to temperature. Thus in the case of saturation state, when the characteristic functions are one-variable functions, the notation of total differentials may be used in the expression

$$\kappa = \frac{c_p}{c_v} = \frac{dh/dT}{du/dT} = \frac{dh}{du}. \qquad (40)$$

The size variation of droplets and bubbles always is coupled with entropy variation, it is no isoentropic process, but a polytropic one. The expression of the isoentropic exponent (40) makes possible to determine the analogue of the polytropic exponent characteristic of real processes. Combining the equations (31), (32) and (40), we obtain

$$n_* = \frac{dh_*}{du_*} = \frac{T \, ds_* + v \, dp_*}{T \, ds_* - p_* \, dv} \qquad (41)$$

as the analogue of the polytropic exponent valid in disperse state, which can be rewritten by means of the equations (16), (38) and (39).

It should be mentioned that the substitution $ds_* = 0$ yields the analogue of the isoentropic exponent given by

$$\kappa_* = -\frac{v \, dp_*}{p_* \, dv} \qquad (42)$$

as can be seen among the results of studies on multiphase systems [10].

In the case of a polydisperse system in which the temperature and size distribution of the disperse phase is nonuniform, an average is to be determined. In this regard there are two different alternatives depending upon the nature of distribution. The distribution function may be either a discrete or a continuous one.

In order to generalize and abbreviate the ensuing investigation let us introduce the notation

$$z_* = s_*; \; f_*; \; u_*; \; h_*; \; g_*; \; r_*, \qquad (43)$$

as a generalized symbol instead of the equations (18)–(23).

On condition that the disperse phase is composed of discrete groups, in each of them the single spherical particles have temperature T_j and radius R_k, besides, the mass M_{jk} represents the total mass of these groups, the average per unit mass of the disperse phase can be determined by

$$\bar{z}_* = \frac{\Sigma_k \Sigma_j z_*(T_j, R_k) M_{jk}}{\Sigma_k \Sigma_j M_{jk}}, \tag{44}$$

where the symbol z_* is to be substituted corresponding to the equation (43), in turn.

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

$$\tilde{z}_* = \frac{\iint z_*(T, R) M \,\mathrm{d}T \,\mathrm{d}R}{\iint M \,\mathrm{d}T \,\mathrm{d}R} \tag{45}$$

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

Till now we dealt with the characteristic functions and some other relationships concerning the disperse phase in one-component systems, independent of its state of aggregation (droplet or bubble). Further on, the differences will be outlined which can be found between one- and two- or more-component systems in view of the disperse phase.

It is known that the behaviour of the interfacial boundary layer is determined by the surface tension which is strongly dependent upon the chemical composition and temperature of the liquid phase, less affected by the size (apart from the range of very minute sizes), and scarcely influenced by the chemical composition of the adjacent noncondensed phase.

It follows from the foregoing that the surface tension in all equations should be taken into account in accordance with the liquid medium referred to the adjacent vapour or gas, independent of which fluid is in disperse state.

This means that the equations deduced for the disperse phase in one-component systems are valid also for that in two- or more-component systems, as to the form, but we have to take into consideration the following.

In a supposed equilibrium the phases of different chemical composition, consisting of chemically non reacting species, penetrate into each other, in consequence of what the liquid phase becomes a solution, and the vapour phase turns to a mixture of vapours. Therefore the solubility of the noncondensed component in the adjacent liquid, as well as, the evaporation of the liquid medium are to be taken into account when determining the surface tension.

Under non-equilibrium conditions, when variation takes place in the droplet or bubble size, respectively, the phase of diminishing mass suffers no change in the chemical composition, while the concentration of the other phase is continuously varied, however, it can be limited by physical and chemical properties of the components.

Consequently, the equations deduced for the disperse phase in one-component systems are valid at two-component systems, too, viz. in their unchanged forms, supposing that the physical quantities depending upon the surface tension will adequately be determined as it was just previously dealt with.

In the case of more-component systems, i.e. if the disperse phase consists of droplets or bubbles which are not of the same chemical composition, the equations deduced for one-component systems are valid only for the single components of the disperse phase.

Under the circumstances let us use the notation $z_*^{(i)}$, $\bar{z}_*^{(i)}$, and $\tilde{z}_*^{(i)}$, instead of the equations (43)–(45), in turn, where the index (i) denotes that the corresponding quantity belongs to the ith component, and the mass of the ith component be represented by M_i. In this case the weighted average of the above-mentioned quantities per unit mass of the disperse phase can be determined either by

$$\bar{\bar{z}}_*^{(\Sigma)} = \frac{\Sigma_i \bar{z}_*^{(i)} M_i}{\Sigma_i M_i}, \tag{46}$$

if the disperse particles are of discrete distribution, or by

$$\tilde{\tilde{z}}_*^{(\Sigma)} = \frac{\Sigma_i \tilde{z}_*^{(i)} M_i}{\Sigma_i M_i}, \tag{47}$$

if the temperature and size distribution is continuous.

In connection with the analogue of Clausius–Clapeyron equation for multiphase systems (39), a phenomenon worth mentioning will be presented which covers the range of theoretical interest and practical importance alike.

The pressure in a vapour bubble necessarily exceeds that of the ambient liquid. Besides, it is known that the Clausius–Clapeyron equation connects the pressure difference to the temperature difference [17, 18], therefore in consequence of the equations (13)–(16) there is no thermal equilibrium between vapour bubbles and the ambient liquid.

In accordance with experimental observations, as the bubble grows evaporation takes place at the bubble boundary, while the temperature and pressure in the bubble are thereby decreased. The reduction of the temperature within the bubble is a consequence of the latent heat requirement of the evaporation which takes place at the vapour–liquid interface, as the bubble grows [19].

This experience can qualitatively be expressed by

$$\operatorname{sgn} \mathrm{d}T = \operatorname{sgn} \mathrm{d}p''_*, \tag{48}$$

in accordance with the Clausius–Clapeyron equation as well as by

$$\operatorname{sgn} \mathrm{d}p''_* = -\operatorname{sgn} \mathrm{d}R, \tag{49}$$

on the one hand, and by

$$\operatorname{sgn} \mathrm{d}p''_* = \operatorname{sgn} \mathrm{d}(\Delta p), \tag{50}$$

on the other.

Under non-equilibrium conditions the bubble always has a radially moving boundary and the *driving force* of this motion is produced by the *temperature difference* between phases [18, 20].

In the case of bubble collapse the temperature difference results in heat outflow what is accompanied by size reduction. Owing to the condensation at the interface not only the bubble radius is decreased, but also the pressure difference between phases and the bubble pressure are increased, in accordance with the equations (48)–(50), while the wall temperature and the surface tension remain practically unchanged [18]. The elevated temperature brings about a more intensive heat outflow, the size reduction reacts upon the *temperature difference increasing* it, the heat outflow will thereby be excited more thoroughly, therefore the temperature variation does not tend to the immediate equalization of the phase temperatures, contrary to all expectation [21].

However, we have to take into account that bubbles do not show necessarily a monotonic size reduction, but the size variation may be of fluctuating character, as it can be observed, too [22, 23]. The possible size fluctuation may be treated as a secondary effect which is superposed on the *primary effect produced by temperature difference.* In spite of this size fluctuation both the temperature and pressure uninterruptedly remain higher in the bubble than in the liquid phase. Thus the temperature difference between phases continues to exist and maintains the *basic tendency of size variation* while yielding the stability on going to smaller and smaller sizes.

It follows from the foregoing that the bubble collapse is a *process of positive feedback.* On the other hand, it can basically be regarded as a realization of the *rocket principle* in the special case of radially moving surface elements of decreasing mass, in the course of which motion a compression work is done what is accompanied by conversion of work to heat. Thus arises the question, how high the bubble temperature can be elevated. In this regard we have nothing else to suppose but the temperature rise goes on until it is affected by the cause maintaining the process.

In the present case this cause is the *growing temperature difference* by which also the *pressure difference* and the pressure itself are increased. It denotes that the vapour bubble would cease to exist at the critical temperature and pressure, if the surface tension decreased with temperature rise of the bubble [21]. Since the wall temperature and surface tension are practically not decreased [18], the pressure and temperature rise in the vapour bubble will exceed the critical values taken in the usual sense. Under the circumstances it would be more correct to call this phenomenon the *modification of the critical state,* what directly follows from that of the saturation state depending upon particle size, too.

This theorem is effectually supported by the main results of some *cavitation studies.* It has been found that the cavitation damage arises primarily from repeated application of high stresses and temperatures of short duration which accompany the bubble disappearance [24]. The high bubble temperature in final state is to be supposed on the strength of the fact that a colour change of the metal surface can be observed at the sites of erosion damage caused by cavitation. The surface erosion and colour change must not be attributed to chemical dissociation in the liquid [24].

Searching for the cause of the cavitation damage we will return to the capillary superpressure given by the expression (11).

In this connection it should be mentioned again that the wall temperature and the surface tension remain practically unchanged [18], thus the variation in surface tension should be attributed to the size variation.

As for this problem, opinions disagree. Using a quasithermodynamic approach Tolman [9] predicted a decrease in surface tension at small sizes and this result is supported by a statistical mechanical treatment due to Kirkwood and Buff [25]. On the other hand Martynov takes the view that surface tension should increase with curvature [26].

As yet there seems to be no direct experimental method for confirmation of these theoretical results but insight into the problem may be gained by returning to a previous assumption taken by Thomson [12]. He is of the opinion that the *variation in surface tension* σ_* *dependent on radius* R *would pass through a minimum.* In the light of this assumption the above-mentioned inconsistency ceases and the partial theoretical results seem to be completed by one another.

Thus come we to the conclusion that in the initial period of bubble disappearance the effect of size variation is stronger than the contrary effect of surface tension variation on capillary super-pressure, i.e. the numerator decreases less than the nominator in the expression (11). In the subsequent period of bubble disappearance the surface tension—beyond its minimum—increases with size decrease, thus the capillary superpressure will be elevated very much what leads to *extremely high values of final pressure and temperature in bubbles.* This is in full agreement with the well-known results of experimental observations that the final pressure at bubble disappearance is very high, it might be as well a large multiple (10^2–10^3-fold) of the critical pressure taken in the usual sense. Such an order of magnitude in final pressure can occur only in the case of an *extremely rapid and considerable increase in surface tension* on going to very minute bubble sizes.

Under the circumstances the temperature equalization of phases is carried out in such a way that the bubble of minute residual mass which is in the modified critical state determined by the final bubble size expands *like explosion* producing thereby a strong shockwave and then mixes with the liquid phase.

It can be observed that the superficial effects become important especially when the bubble is near the point of complete collapse [18], in other words, in the submicroscopic range.

Finally, it should be mentioned that the usual thermodynamic diagrams of two dimensions (pressure vs temperature, pressure vs specific volume, temperature vs specific entropy, specific enthalpy vs specific entropy etc.) are valid for bulky liquid and vapour only. The diagrams in question referred to droplets and bubbles are arranged in space and can be deduced from the planar ones, if we complete them by the spatial third co-ordinate $1/R$. In such co-ordinate systems the original diagrams become the reference planes where $1/R = 0$, so they remain valid for bulky phases, in other words, the superficial terms referred to disperse particles of finite radius disappear in the modified equations.

Though the effects of the translatory motion not dealt with are of great importance, they do not change the character of the processes in question but, of course, their time dependence is thereby varied.

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LES FONCTIONS CARACTERISTIQUES DES SYSTEMES DE FLUIDES A PLUSIEURS PHASES ET L'INTERPRETATION THERMODYNAMIQUE DU COLLAPSUS DES BULLES DE VAPEUR

Résumé—On étudie les effets de l'interface de phase, et de la tension interfaciale dans les systèmes de fluides multiphasiques. On évalue la modification de l'entropie, de l'énergie libre, de l'énergie interne, de l'enthalpie, de l'enthalpie libre et leurs différentielles, à la fois pour des gouttelettes et des bulles de vapeur de température uniforme ou non et avec une distribution en taille. L'étude tient compte aussi de la chaleur latente, de l'équation de Clausius–Clapeyron, de l'exposant polytropique adapté à l'état dispersé. Les relations déduites pour des systèmes à un seul composant sont généralisées pour des systèmes à deux ou trois composants. On montre que lors de la réduction de la taille de la bulle, la température de la vapeur et la pression s'élèvent bien au dessus des valeurs critiques connues au sens habituel, car dans l'état de saturation la courbe de coexistance et l'état critique sont modifiés par la dimension submicroscopique de la bulle. On explique l'interdépendence entre l'annihilation de la bulle et les dégats par cavitation.

DIE CHARAKTERISTISCHEN FUNKTIONEN MEHRPHASIGER FLUIDSYSTEME UND DIE THERMODYNAMISCHE INTERPRETATION DES ZUSAMMENBRECHENS VON DAMPFBLASEN

Zusammenfassung—Es werden die Einflüsse von Phasengrenzfläche und Oberflächenspannung in mehrphasigen Fluidsystemen untersucht. Für Tropfen und Dampfblasen mit gleichförmiger und ungleichförmiger Temperatur und Größenverteilung werden die Änderungen der Entropie, der freien Energie, der inneren Energie, der Enthalpie und der freien Enthalpie und deren Differentiale abgeleitet. Die Untersuchung liefert außerdem die latente Wärme, die Clausius-Clapeyron-Gleichung und den Polytropenexponenten für den dispersen Zustand. Die für Einkomponenten-Systeme abgeleiteten Beziehungen werden auf zwei- und Mehrkomponenten-Systeme erweitert. Es wird gezeigt, daß im Verlauf der Abnahme der Blasengröße sowohl die Dampftemperatur wie der Druck erheblich über die normalen kritischen Werte ansteigen, da der Sättigungszustand, die Koexistenzkurve und der kritische Zustand infolge der submikroskopischen Blasengröße wesentliche Änderungen erfahren. Außerdem wird der Zusammenhang zwischen Blasenkollaps und Kavitationsschäden erklärt.

ХАРАКТЕРИСТИЧЕСКИЕ ФУНКЦИИ МНОГОФАЗНЫХ ЖИДКИХ СИСТЕМ И ТЕРМОДИНАМИЧЕСКОЕ ОПИСАНИЕ РАЗРУШЕНИЯ ПУЗЫРЬКОВ ПАРА

Аннотация — Исследуются эффекты на границе раздела фаз и поверхностного натяжения в многофазных жидких системах. Выражения для энтропии, свободной энергии, внутренней энергии, энтальпии, свободной энтальпии и их дифференциалов выведены для капелек и для пузырьков пара при равномерном и неравномерном распределении по размерам и температурам. В результате исследования определена также скрытая теплота парообразования и показатель политропы, рассчитанный из дисперсного состояния. Соотношения, выведенные для однокомпонентных систем, обобщены для систем с двумя и более компонентами. Показано, что при уменьшении размера пузырька температура пара и давление намного превышают критические значения, взятые в обычном смысле, поскольку состояние насыщения и критическое состояние существенно модифицированы из-за наличия пузырьков субмикроскопических размеров. Объяснена также взаимосвязь между аннигиляцией пузырька и кавитационными повреждениями.