THERMODYNAMIC FUNCTIONS FOR DISPERSE TWO-PHASE FLUID SYSTEMS†

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Interface effects are investigated. Modified thermodynamic functions and equations are derived for droplets and vapor bubbles of a two-phase system.

The description of thermodynamic processes in disperse liquid systems requires knowledge of the instantaneous states of the phases. Thermodynamic functions can be used to describe not only the steady state of equilibrium systems, but also the instantaneous states of nonequilibrium systems and the local states of their separate homogeneous parts. We now propose to carry out a theoretical investigation of the state of two-phase liquid systems in which surface tension affects the surface thermodynamic functions.

Surface tension can be neglected only in the case of a simple horizontal phase interface, for which surface tension does not elicit an excess pressure in either phase, or when the curvature of the interface is small and the mass of the interfacial boundary layer is small in comparison with the total mass of the system.

In the study of two-phase systems it must be decided which phase is subjected to surface tension effects. If one of the phases is disperse, then it is clearly the state of that phase which is principally affected by surface tension. Consequently, the variations can be attributed mainly to the disperse phase, whereas the coherent phase experiences almost no variations [1]. The logical choice, then, is the disperse phase, which is the option taken in the present study.

Our investigation is based on an analysis of the behavior of disperse particles in one-component two-phase fluid systems and then of situations in which the disperse phase comprises two or more components.

The fundamental thermodynamic equations relating the thermodynamic functions are as follows:

$$U = F + TS,$$

$$H = U + pV,$$

$$G = F + pV.$$

For the case in which these thermodynamic functions refer to a single disperse particle surrounded by a coherent phase (such as a droplet in a vapor atmosphere or a bubble in a liquid volume) we introduce the notation

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

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

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

If F is the free energy of a definite fluid element of the same mass as a droplet or bubble without a phase interface, then with the latter present and all other conditions being equal, the free energy of the given element assumes the form

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

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where A is the area of the interface surrounding the disperse particle and σ_* is the surface tension [1-3]. The entropy is given by the expression [3,4]

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

which upon substitution into Eq. (4) yields

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

where S_* is the entropy with the interface present [1,2,5].

Substituting Eqs. (4) and (5) into (1), we obtain the internal energy of a single disperse-phase particle [1,2,5]:

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

It is well known that the pressure of particles surrounded by a liquid or vapor in a two-phase fluid system is always greater than the pressure of the surrounding phase; we denote the excess by Δp. However, the pressure in the surrounded particles, besides differing from the external pressure, also differs from the saturation pressure corresponding to their intrinsic temperature, by an amount Δp_* to be determined later.

Under the foregoing conditions the enthalpy expression (2) and the free-enthalpy expression (3) take the respective forms

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

and

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

as deduced earlier [6] in a determination of the quantity of work required to form the surface of a bubble [7,8].

The surface tension is regarded in the majority of cases as a function of the temperature; this assumption is precisely valid only in the case of a horizontal plane interfacial surface.

When droplets and bubbles of sufficiently small radius are investigated, they are assumed to be spherical. In the present state of the theory the influence of particle size on surface tension is customarily taken in the approximation

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

where δ is a quantity expressing intermolecular force effects and can be treated approximately as a constant having a value between 10^{-10} and 10^{-9} m [5,9,10]. In the case of very small particle radii the approximate expression (9) is not sufficiently accurate [9,11].

Thermodynamic analysis yields the equation

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

for the interdependent variables investigated, where δ can no longer be regarded as a constant. Moreover, it is important to be aware of the probability that the given quantity can change sign and thus imply a minimum surface tension as smaller and smaller radii are considered [12].

The indicated behavior of the surface tension is particularly important in connection with cavitation effects, as will be discussed below.

Referring to the above-mentioned pressure differences, we know from the Laplace theorem that the capillary excess pressure inside a spherical disperse-phase particle over the ambient pressure of the surrounding medium is

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

Also, the vapor pressure is frequently expressed on the basis of Kelvin's reasoning as

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

where the upper sign (+) refers to a droplet, and the lower sign (—) to a bubble [2,13-15]. This expression is derived from the following relation due to Taylor:

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

In the latter equation the surface tension must be estimated as above, and the radius as in earlier works [2,5,15,16].

This means that the pressure in a bubble can be obtained at once from Eq. (13), but to determine the pressure in droplets the equation must be augmented with the pressure difference (11) between phases. Therefore, the pressure in a single droplet or bubble can be determined from the relation

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

and, introducing the notation

$$Y = \frac{2\sigma_*}{p_s R} \cdot \frac{v'}{v'' - v'}\,, \tag{15}$$

we obtain

$$p_* = p_s \exp Y + \frac{(1 \pm 1)\,\sigma_*}{R}\,, \tag{16}$$

where the upper sign (+) refers to a droplet, and the lower sign (—) to a bubble; thus, in the latter case the last term on the right-hand side of the expression vanishes. The exponential can be either positive (for a droplet) or negative (for a bubble) [15,16].

On the basis of Eq. (16) the difference between the saturation pressure and the pressure in a droplet or bubble is given by the expression

$$\Delta p_* = p_s - p_* = p_s(1 - \exp Y) - \frac{(1 \pm 1)\,\sigma_*}{R}\,, \tag{17}$$

in which the sign convention is the same as above.

It follows from Eqs. (13)-(16) that when droplets disperse in a one-component system, the pressure in both phases exceeds the saturation pressure, but when bubbles disperse in the same kind of system the pressure in both phases becomes less than the saturation pressure. In other words, if a two-phase disperse system is in thermal equilibrium, then in conventional terminology both phases are either supercooled (droplets in a vapor atmosphere) or superheated (bubbles in a liquid volume). Actually, Eqs. (13)-(16) more nearly signify that not only the thermodynamic functions, but also the terms describing the saturation state itself, vary under these conditions, because the usual definition of the saturation state whereby the pressure depends exclusively on the temperature is valid not only in general, but also in the special case $R = \infty$, and if the latter does not hold, the saturation state is determined not only by the temperature, but also by the surface tension and particle size. The instantaneous saturation state of a droplet or vapor bubble can be identified with the fact that negligibly small heat transfer is necessarily accompanied by phase changes.

The thermodynamic functions per unit mass of the disperse phase can be obtained in a special form as follows.

Given the condition that the system is monodisperse, i.e., the temperature and size distribution in the disperse phase is uniform, we use Eqs. (4)-(8), substituting the spherical surface area and volume as well as the pressure difference (17) therein, and then, referring everything to the mass of a single droplet or bubble, obtain the corresponding functions

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

$$f_* = f + \frac{3v\sigma_*}{R} = g - v\left(p_s - \frac{3\sigma_*}{R}\right), \tag{19}$$

$$u_* = u + \frac{3v(\sigma_* - T\partial\sigma_*/\partial T)}{R} = Ts + g - v\left(p_s - \frac{3(\sigma_* - T\partial\sigma_*/\partial T)}{R}\right), \tag{20}$$

$$h_* = h - v\left(p_s(1 - \exp Y) - \frac{(4 \pm 1)\sigma_* - 3T\partial\sigma_*/\partial T}{R}\right) =$$

$$= Ts + g - v\left(p_s(1 - \exp Y) - \frac{(4 \pm 1)\sigma_* - 3T\partial\sigma_*/\partial T}{R}\right), \tag{21}$$

$$g_* = g - v\left(p_s(1 - \exp Y) - \frac{(4 \pm 1)\sigma_*}{R}\right), \tag{22}$$

in which the upper sign (+) refers to a droplet, and the lower sign (—) to a bubble, while the sign of the exponential is determined as in Eqs. (15) and (16).

Having found the enthalpy, we can determine the latent heat with allowance for surface tension.

In the conventional latent-heat expression

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

the effects of surface tension and capillary excess pressure are disregarded. Taking those effects into account, we need to examine two cases, depending on the nature of the two-phase system.

If droplets disperse with a uniform temperature and size distribution in a vapor atmosphere, then the latent heat per unit mass of liquid phase can be written

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

If a liquid volume contains bubbles with a uniform temperature and size distribution, then the latent heat per unit mass of vapor phase is given by

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

On the basis of the foregoing relations two kinds of capillary latent heat can be described by the expression

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

in which the upper signs (+) refer to droplets in a vapor atmosphere, and the lower signs (—) to bubbles in a liquid volume.

It is seen that these two kinds of capillary latent heat differ from the usual form and obey the double inequality

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

under the condition that the temperature and radii of the disperse-phase particles are identical. This means that, contrasted with the usual latent heat, evaporation of the liquid requires less energy if droplets are formed and, on the other hand, more energy is released in condensation of the vapor phase if it consists of bubbles.

The foregoing considerations suggest apt definitions for the differentials of the thermodynamic functions for disperse particles.

Thus, the differentials of the principal thermodynamic variables (1)-(3) are specified in the form

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

whereupon the Gibbs — Duhem relation

$$S_*dT - Vdp_* + Mdg_* = 0 \tag{24}$$

can be used to define the differentials of the potential functions as

$$dF_* = -p_*dV - S_*dT + g_*dM, \quad dU_* = TdS_* - p_*dV + g_*dM, \qquad (25), (26)$$

$$dH_* = TdS_* + Vdp_* + g_*dM, \quad dG_* = Vdp_* - S_*dT + g_*dM, \tag{27), (28}$$

and for the specific values, when the Gibbs — Duhem relation has the form

$$s_*dT - vdp_* + dg_* = 0, \tag{29}$$

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

$$df_* = -p_*dv - s_*dT, \quad du_* = Tds_* - p_*dv, \tag{30), (31}$$

$$dh_* = Tds_* - vdp_*, \quad dg_* = vdp_* - s_*dT. \tag{32), (33}$$

These equations are seen to differ from their conventional counterparts only insofar as they contain s*, ds*, p*, and dp* rather than s, ds, p, and dp. The entropy s* and pressure p* for the disperse state have already been found, so their differentials are readily determined. Differentiating expressions (16) and (18) with respect to T and the radius R, we obtain

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

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

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

$$\frac{\partial p_*}{\partial R} = p_s \frac{\partial Y}{\partial R} \exp Y + (1 \pm 1) \frac{\partial}{\partial R} \cdot \frac{\sigma_*}{R}. \tag{37}$$

The double sign convention is as explained above.

For the given conditions the entropy differential is defined as

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

whereas the pressure differential in disperse particles can be defined in the form

$$dp_* = (dp_s + p_s dY) \exp Y + (1 \pm 1)\, d\, \frac{\sigma_*}{R}, \tag{39}$$

which may be regarded as an analog of the Clausius — Clapeyron equations

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

for the disperse state, because the pressure p does not depend on the temperature alone.

Once the differentials have been defined, we can define the polytropy exponent n* for the disperse state.

The isentropy exponent actually denotes the ratio of the isobaric to the isochoric specific heat, but these two types of specific heat represent the ratios of the enthalpy and internal energy to the temperature. Thus, in the saturation state, for which the thermodynamic functions are functions of one variable, the total differentials can be used in the expression

$$\varkappa = \frac{c_p}{c_v} = \frac{dh/dT}{du/dT} = \frac{dh}{du}. \tag{40}$$

The variation of the radii of droplets and bubbles is always related to the entropy variation, which is neither an isentropic nor a polytropic process. The expression (40) for the isoentropy exponent enables us to define a characteristic analog of the polytropy exponent for real processes. From Eqs. (31), (32), and (40) we obtain

$$n_* = \frac{dh_*}{du_*} = \frac{Tds_* + vdp_*}{Tds_* - p_*dv}. \tag{41}$$

Since the analog of the polytropy exponent is valid for disperse states, it may be determined with the help of (16), (38), and (39).

It should be recalled that the substitution $dS_* = 0$ yields the analog of the isentropy exponent

$$\varkappa_* = -\frac{vdp_*}{p_* dv}, \tag{42}$$

which has already been mentioned in the literature on two-phase systems [10].

In the case of a polydisperse system, where the temperature and size distribution in the disperse phase is not uniform, averaging is necessary. Two averaging techniques are used, depending on the nature of the distributions. The distribution functions can be either discrete or continuous.

To generalize and abbreviate the subsequent calculations we introduce the notation

$$z_* = s_*;\ f_*;\ u_*;\ h_*;\ g_*;\ r_* \tag{43}$$

as generalized symbols for Eqs. (18)-(23).

Given the condition that the disperse phase consists of discrete groups, in each of which the individual spherical particles have temperature T and radius r_* and the mass M denotes the total mass of the groups, the formula for averaging per unit mass of the disperse phase is

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

where one of the variables of Eq. (43) is inserted in place of z_*.

For the case in which the disperse phase contains spherical particles with a continuous temperature and size distribution, analogously, the formula

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

gives the averages of the indicated functions per unit mass of the disperse phase.

So far we have discussed the thermodynamic functions and certain other relations for the disperse phase in one-component systems irrespective of their aggregate state. Below we indicate the differences that can be established between one- and two-component systems with respect to the disperse phase.

It is well known that the behavior of the interphase boundary layer is determined by surface tension, which depends significantly on the chemical composition and temperature of the liquid phase, to a lesser degree on the particle size (apart from extremely small sizes), and almost not at all on the chemical composition of the contiguous uncondensed phase..

The foregoing considerations imply that surface tension must be included in all equations for the medium that refer to the contiguous vapor or gas, regardless of which liquid is in the disperse state.

This means that the equations derived for the disperse phase in one-component systems are also valid in general for systems of two or more components, but the following must be borne in mind concerning their form.

Given the assumption of equilibrium, phases having different chemical compositions interpenetrate, so that the liquid phase becomes a solution and the vapor phase a mixture of vapors. Therefore, in determining the surface tension it is essential to consider both the solubility of the uncondensed component in the surrounding liquid as well as evaporation of the liquid.

In the nonequilibrium case, where the dimensions of the droplets or bubbles vary, the decreasing-mass phase does not undergo variations in chemical composition, whereas the concentration of the other phase varies continuously, although this transition can be limited by the physical and chemical properties of the components.

Consequently, the equations derived for the disperse phase in one-component systems are also valid for two-phase systems in the same form, subject to the condition that physical variables depending on the surface tension are defined with sufficient accuracy, as discussed above.

In the case of multicomponent systems, i.e., when the disperse phase consists of droplets or bubbles of dissimilar chemical composition, the equations derived for one-component systems are valid only for the individual components of the disperse phase.

Under these conditions we use the symbols $z_*^{(i)}$, $\bar{z}_*^{(i)}$, and $\tilde{z}_*^{(i)}$ in Eqs. (43)-(45), the superscript (i) denoting that the given variable refers to the i-th component, and we denote the mass of the i-th component by M_i. In this case the weighted averages of the above-mentioned variables per unit mass of the disperse phase can be defined as

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

for particles having discrete temperature and size distributions, or as

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

for continuous distributions.

We complement the foregoing discussion with an analysis of a special case of theoretical and practical significance.

The pressure in a vapor bubble necessarily exceeds the pressure of the surrounding liquid. It is also known that the Clausius — Clapeyron equation relates the pressure difference to the temperature difference [17,18], so that Eqs. (13)-(16) do not describe thermal equilibrium between vapor bubbles and the surrounding liquid.

Experimental studies indicate that as bubbles grow evaporation takes place at the bubble boundary, the temperature and pressure in the bubble interior decreasing. The temperature inside the bubble decreases due to evaporation at the vapor — liquid interface with growth of the bubble [19].

These experimental results can be characterized by the relation

$$\operatorname{sgn} dT = \operatorname{sgn} dp''_* \tag{48}$$

or equivalently, in accordance with the Clausius — Clapeyron equation, in the form

$$\operatorname{sgn} dp''_* = -\operatorname{sgn} dR, \tag{49}$$

or even in the alternative form

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

In the nonequilibrium state the bubble boundary always moves radially due to the temperature difference between phases [18,20].

When bubbles implode, the temperature difference produces a heat sink accompanied by a reduction in size. As a result of condensation at the phase interface, not only does not bubble radius diminish, but the pressure difference between phases and the bubble pressure increase according to Eqs. (48)-(50), whereas the wall temperature and surface tension remain virtually unchanged [18].

The increase in temperature elicits a stronger heat sink, and the size reduction promotes an increase in the temperature difference, causing the heat sink to be more active, so that, contrary to all expectations, the temperature variation does not produce rapid temperature equalization between phases [21].

It must be realized, however, that the reduction in bubble size does not necessarily have a monotonic behavior, rather it can exhibit a fluctuation character [22,23]. The possible size fluctuations can be regarded as a secondary process superimposed on the primary effect induced by the temperature difference. Despite this variation of size, both the temperature and pressure in the bubbles are always higher than in the liquid phase. Consequently, the temperature difference between phases is preserved and gives rise to a gradual reduction in size.

It follows from the foregoing considerations that the implosion of bubbles is a positive feedback process. On the other hand, this effect can be regarded as a realization of the reaction principle for the special case of radially moving elements of a surface with diminishing mass. Here work is done in compression, accompanied by heat release. It is logical to inquire, therefore, how much the bubble temperature can increase. Inasmuch as this question cannot be answered precisely, we have no alternative but to assume that the temperature increases until it is no longer subjected to the influence of the primary cause of the process.

In the given situation, that cause is the growing temperature difference, for which the pressure difference and the pressure itself increase. This means that a vapor bubble would cease to exist if the surface tension were to decrease with increasing bubble temperature [21]. Inasmuch as the wall temperature and surface tension scarcely decrease at all [18], the increasing pressure and temperature of the vapor bubble exceed the usual critical values. Under the conditions that we have stated above it would be more correct to refer to this effect as a modification of the critical state, as is inferred from the fact that the saturation state also depends on the particle size.

The latter hypothesis is in fact confirmed by the fundamental results of cavitation studies. It has been found that cavitation is induced primarily by repeated short-term high pressures and temperatures accompanying the implosion of bubbles [24]. The high temperature of a bubble in the final state is postulated on the basis of the fact that at cavitation-induced erosion pits a change in color of a metal surface can be observed. The surface erosion and color change cannot be attributed solely to chemical dissociation of the liquid [24].

In looking for the causes of cavitation erosion we refer to the capillary excess pressure described by expression (11).

We reiterate in this connection that the wall temperature and surface tension remain practically unchanged [18], so that the variations in surface tension must be identified with size variation.

Opinions differ with regard to this problem. Using a quasithermodynamic approach, Tolman [9] predicts a reduction in surface tension for small bubble sizes, and this result is corroborated by the statistical treatment of Kirkwood and Buff [25]. On the other hand, Martynov [26] assumes that the surface tension must increase with the curvature.

A direct experimental method has not been devised to date for confirmation of these theoretical results, but insight into the problem is afforded by a hypothesis of Thomson and Thomson [12]. The latter assume that the curve of the surface tension σ_* as a function of the radius R passes through a minimum. Accordingly, the above-indicated cases and partial theoretical results appear to complement one another.

We therefore arrive at the conclusion that in the initial period of bubble implosion the size variation exerts a stronger influence than surface tension on the capillary excess pressure, i.e., the numerator in expression (11) decreases more slowly than the denominator. In the later period of bubble implosion the surface tension (above the minimum) increases inversely as the size, whereupon the capillary excess pressure increases so rapidly as to produce extremely high values of the final pressure and temperature in the bubbles. This inference is completely consistent with the well-known experimental results that if the final pressure in bubble implosion is very high, it can be several orders of magnitude (10^2 to 10^3) greater than the normal critical pressure. This order of magnitude of the final pressure can occur only in the event of an ultimately rapid and sizable increase in the surface tension in transition to very small bubble sizes.

Under the given circumstances temperature equalization of the phases takes place in such a way that a bubble of small residual mass existing in the altered critical state is determined by the final radii, expands instantaneously, thereby generating a strong shock wave, and then mixes with the liquid phase. It can be observed that surface effects take on special importance when a bubble is close to complete implosion [18], i.e., when its radius is less than a few microns.

It is important to mention, finally, that the usual two-dimensional thermodynamic diagrams (pressure versus temperature, pressure versus specific volume, temperature versus specific entropy, specific enthalpy versus specific entropy, etc.) are valid only for the liquid and vapor volumes. Diagrams representing droplets and bubbles have been investigated in three-dimensional space and can be derived from the two-dimensional diagrams by adding a third coordinate 1/R to them. In such coordinate systems the original diagrams become the initial planes, in which $1/R = 0$, and so remain valid for the volume phases; in other words, surface terms referring to disperse particles of finite radius vanish in the modified equations.

Although the translational motion effects ignored here are of considerable importance, they do not alter the nature of the investigated processes, but their time dependence does of course change accordingly.

NOTATION

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; n, polytropy exponent; p, pressure; Δp, pressure difference; p_s, saturation pressure; R, radius of disperse particles; r, latent heat of vaporization; S, entropy; s, specific entropy; T, absolute temperature; U, internal energy; u, specific internal energy; V, volume; v, specific volume; Y, exponent of deviation from saturation state; z, arbitrary function; δ, quantity characterizing intermolecular forces; ϰ, isentropy exponent; σ, surface tension; prime refers to the liquid phase of a vapor; double prime refers to the vapor phase; asterisk refers to the disperse state.

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