MODIFICATION OF THE CHARACTERISTIC FUNCTIONS IN DISPERSED TWO-PHASE SINGLE-COMPONENT SYSTEMS. I

E. Pattantyush

UDC 536.7

The characteristic functions and certain quantities of state are modified in the presence of an interphase boundary of separation and surface tension.

A precise knowledge of the characteristic functions and the quantities of state plays an important role when describing certain thermodynamic relations in heat- and mass-transfer processes.

According to the theorem on surface tension, the characteristic functions and certain quantities of state differ from their simple algebraic sum, corresponding to individual phases without a surface of separation, all other conditions being equal, i.e., their total mass, temperature, and pressure are identical. Consequently, in order to accurately describe two-phase systems, the additional effects of surface tension also should be taken into account. They can be neglected only in the case when the following simplifying **assumptions** are valid:

a) the mass of the interphase boundary layer is very small in comparison with the total mass of the whole system;

b) surface tension does not cause an excess pressure in one of the phases; in other words, the curvature of the interphase boundary of separation is relatively insignificant.

During an investigation of two-phase systems, the problem arises of which phase is the carrier of the changes caused by surface tension. In the case when one of the phases is dispersed, it can be **clearly seen** that the effect of surface tension is predominantly on the state of this phase; consequently, these changes can be referred to the dispersed phase while the coherent phase is subjected to almost no changes whatsoever [1].

Based on this assumption relative to the characteristic functions, we shall try to reduce the investigation of two-phase, single-component systems to an investigation of the dispersed phase. This consideration can simplify transition to two or more component systems.

The well-known relations of the characteristic functions are determined in the following way:

$$E = F + TS,$$

$$H = E + pV,$$

$$G = F + pV.$$

In the case when these characteristic functions refer to a single dispersed particle, surrounded by a coherent phase of the same chemical composition, as, for example, a drop in a vapor atmosphere or a bubble in a volume of liquid, we can write

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

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

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

If the free energy F is referred to a definite part of the medium without a surface of separation, then for one and the same mass the modified free energy can be expressed as

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Budapest. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol.31, No.1, pp.73-78, July, 1976. Original article submitted October 24, 1974.

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

and it is increased only due to the interphase surface of separation [1-3].

The entropy evolved from the free energy [3,4] is represented in the form

$$S = -\frac{\partial F}{\partial T}, \tag{5}$$

and, in consequence of this definition, by means of Eq. (4) we obtain

$$S_* = S - A\frac{d\sigma}{dT}, \tag{5'}$$

the entropy modified by the presence of the interphase surface of separation [1,2,5].

Substituting (4) and (5) into (1), we obtain the internal energy of a surrounding particle of the dispersed phase:

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

It is known that for the surrounding liquid and particles of vapor in a two-phase system there is always an excess pressure (Δp) in comparison with the pressure of the surrounding medium. However, the pressure inside a surrounded particle differs not only from the pressure of the surrounding medium, but also from the pressure of the saturated vapor, corresponding to its temperature (Δp_*) [2,6-9].

This fact permits the other characteristic functions, up to now not found, also to be determined.

With these conditions, the enthalpy (2) assumes the form

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

and the free enthalpy (3) is

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

in accordance with the work necessary for creating a bubble surface [10,11].

When investigating drops and bubbles, it is assumed, as a rule, that they have a spherical shape. According to Laplace's theorem, the capillary excess pressure inside a spherical particle of the dispersed phase is equal to

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

This formula was modified by Kelvin by assuming that the vapor pressure differs from the saturated vapor pressure in accordance with the usual approximation by

$$\Delta p'' = p_s - p'' = \mp\frac{2\sigma}{R}\,\frac{\rho''}{\rho' - \rho''}, \tag{10}$$

where the upper sign (—) refers to the drop and the lower sign (+) refers to the bubble [2,6,7,9].

This means that the difference between the saturated vapor pressure and the pressure in the bubble can be found from Eq. (10), while in order to determine the difference between the saturated vapor pressure and the pressure in the drop Eq. (10) must be supplemented by the pressure difference between the phases, Δp [Eq. (9)]. Based on this addition, the difference between the pressure inside the dispersed particles of both types and the saturated vapor pressure can be found by the formula

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

where the signs must be the same as shown above, and the density ρ in the denominator always refers to the dispersed phase.

It can be seen from Eqs. (9)-(11) that for the case of a drop the pressure in both phases exceeds the saturated vapor pressure, and, conversely, in the case of bubbles, a pressure difference is observed in both phases. In other words, if a two-phase single-component medium were to exist in thermal equilibrium, then both phases would be either underheated (drops in an atmosphere of vapor) or superheated (bubbles in a volume of liquid) in accordance with the usual terminology.

However, the problem is rather that under these conditions the concept of the state of saturation itself also is modified, while the usual definition of the state of saturation, according to which the pressure of saturation depends exclusively on the temperature, is valid only in the special case when $R = \infty$, for the violation of which the effects of surface tension and the dimensions must be taken into account also. The instantaneous state of saturation of a drop or a bubble of vapor, respectively, can be identified with the fact that an infinitesimal heat transfer is accompanied by a phase change.

The characteristic functions per unit mass of dispersed phase in singular form can be obtained from Eqs. (4)-(8) by the substitution of a spherical surface and volume, and also from the difference of the pressures [Eq. (11)] by partition of the mass of a unit drop or bubble, respectively. With the condition that the system by nature is monodisperse, i.e., the distribution of the temperature and size of the dispersed phase is uniform, all these operations lead to the following functions:

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

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

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

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

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

among which the upper sign (+) in Eqs. (15) and (16) refers to the drop and the lower sign (−) refers to the bubble.

The well-known definition of latent heat

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

does not take into account the effect of surface tension and capillary excess pressure. If this effect is taken into account, then we obtain two variants, depending on the nature of the two-phase system.

If the drops are dispersed in a vapor atmosphere, then with a uniform temperature and size distribution the latent heat per unit mass of liquid phase is defined as

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

In the case when there is a uniform distribution of temperature and size of drops in a volume of liquid, the latent heat per unit mass of vapor phase can be found as

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

Based on these relations, both types of capillary latent heat can be described by means of the usual formula

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

where the upper signs refer to drops and the lower signs refer to bubbles.

It can be seen that the two types of latent heat in the capillaries differ from the normal latent heat according to

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

for the condition that the temperature and radii are equal. In other words, for vaporization of the liquid phase a smaller quantity of heat is required in the case of formation of drops, on the one hand, but, on the other hand, during condensation of the vapor phase with the formation of bubbles a larger quantity of energy is released in comparison with the normal latent heat.

If the system is polydisperse, i.e., if the temperature and radii distributions are nonuniform in the dispersed phase, then the average value must be determined.

There are two different alternatives in this relation depending on the nature of the distribution. The distribution functions may have a discrete or continuous nature.

With the condition that the dispersed phase consists of discrete groups, in each group single spherical particles have a temperature T_i and radius R_j, and mass M_{ij} is the total mass of these groups, then the average value per unit mass of dispersed phase can be found from the formula

$$\bar{z}_* = \frac{\Sigma_j \Sigma_i z_*(T_i,\ R_j)\, M_{ij}}{\Sigma_j \Sigma_i M_{ij}}, \tag{18}$$

in which the value of $z_* = f_*$, s_*, e_*, h_*, g_*, and r_* is substituted from Eqs. (12)-(17).

Similarly, if the dispersed phase contains spherical particles with a continuous temperature and radii distribution, then the formula

$$\bar{z}_* = \frac{\iint z_*(T,\ R)\, MdTdR}{\iint MdTdR} \tag{19}$$

gives the average of the above-mentioned functions per unit mass of the dispersed phase.

Up to now we have been concerned with the characteristic functions of the dispersed phase, independently of the state of aggregation (of the drops or bubbles) but, obviously, the corresponding physical quantities of the coherent phase must be taken into account also, i.e., the weighted mean must be determined when describing the complete two-phase system.

The surface tension in the majority of cases is assumed to be a temperature function, which is, effectively, as for the case of a simple horizontal surface. When investigating drops and bubbles, they are usually assumed to be of spherical shape, and the effect of curvature can be taken into account by using in place of the usual formula for the surface tension the formula

$$\sigma_* = \frac{R}{R+2C}\,\sigma, \tag{20}$$

where C is an empirical constant, equal to 10^{-10}–10^{-9} m, as shown in [5,12,13].

Taking this function and its quotient from differentiation,

$$\frac{\partial \sigma_*}{\partial T} = \frac{R}{R+2C}\,\frac{\partial \sigma}{dT},$$

Eqs. (4)-(17) remain unchanged in their form, except for a small deviation

$$R_* = R + 2C,$$

which must be substituted in them in place of the radius R.

In the case of extremely small dimensions (radii), this effect, if necessary, can be taken into account also.

NOTATION

A, surface area of the phase interface; C, a 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 a drop or bubble; r, latent heat of vaporization; S, entropy; s, specific entropy; T, temperature; V, volume; z, general function; ρ, mass density; σ, surface tension; a single prime (') refers to the liquid phase, a double prime ("), to the vapor phase, and an asterisk (*), to the dispersed state.

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THERMOCONVECTIVE WAVES IN A HORIZONTAL BOUNDED LAYER OF AN INCOMPRESSIBLE FLUID

E. F. Nogotov and A. K. Sinitsyn

UDC 536.25

The propagation of finite-amplitude thermoconvective waves in a horizontal fluid layer with rigid boundaries is investigated.

In liquids with a vertical temperature gradient ($\nabla T \downarrow\downarrow g$), as was first shown in [1,2], it is possible for weakly attenuating thermoconvective waves (TCW) to propagate. In [3,4], accurate analytic solutions were obtained for the propagation of small-amplitude TCW excited by temperature oscillations on the vertical wall of a semibounded layer with free edges. The region of weak attenuation of the TCW was determined, the spectral composition of the TCW was investigated, and amplitude and phase characteristics were obtained.

In [5-7], TCW were investigated in fluid layers with rigid boundaries, examining a number of properties of TCW propagation against a background of mechanical equilibrium of the medium and also in conditions of developed natural convection.

In [5, 7], the propagation of periodic temperature perturbations in an air-filled rectangular horizontal cavity (150 × 50 × 11.7 mm) uniformly heated from below was studied experimentally in the frequency range $\omega = 10^{-2}$-10^{-4} sec^{-1}. The amplitude of the temperature oscillations on the side wall did not exceed 10% of the vertical temperature drop. In [6], numerical calculations were carried out for a region of higher frequencies, approximately an order of magnitude larger than the upper limit achieved in the experiment; in this case, the amplitude of the exciting oscillations chosen was half the temperature drop over the height of the layer.

In the present work, the investigation of TCW in bounded fluid layers is continued. Methods of mathematical modeling are used to study the effect of the exciting wave amplitude on TCW propagation and to elucidate possible mechanisms of TCW propagation for different relations between the amplitude of the temperature oscillations on the side wall and the vertical temperature drop in the layer.

Physical experiments [5,7] have shown that TCW propagation proceeds against a background of a two-dimensional cyclic convective structure. As a result, it is possible to limit theoretical investigations to a two-dimensional model, considering TCW in a rectangular region corresponding to a vertical cross section of the layer perpendicular to the axes of the convective cycle.

Mathematical expressions for TCW propagation may be written using the Boussinesq equations [8]. This system of equations contains the Prandtl (Pr), Grashof (Gr), and Rayleigh (Ra) numbers, as well as ω, the frequency of the temperature oscillations on the side wall, and the parameter α characterizing the relation between the amplitude of these oscillations and the vertical temperature drop in the layer [6]. The Grashof number is determined by the total temperature drop in the layer ($|\gamma d| + A_0$) and the Rayleigh number solely by the temperature drop over the height of the layer (γd).

A. V. Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol.31, No.1, pp.79-85, July, 1976. Original article submitted June 16, 1975.

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