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THE CHANGE IN PHASE OF A FLUID CONSIDERED AS COMPOSED OF MOLECULE CLUSTERS

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Abstract—In the present paper the existence of molecule clusters is assumed *a priori*, showing that the mean statistical mass of a cluster depends on the gas parameters of state, while the mean kinetic energy of clusters is proportional to the measured temperature, and the kinetic energy per unit of volume—to the measured gas pressure. The concept of temperature and pressure detectability has been introduced and an expression for the change-in-phase detectability factor derived. In addition, expressions for the saturation pressure and the mean number of molecules per cluster have been derived as functions of saturation temperature. Finally, a model of vaporization has been proposed and an expression for the limiting liquid superheat derived. The agreement of all these expressions with the experimental results proves to be almost perfect.

NOMENCLATURE

A,	surface area [m^2];
C,	constant of integration;
c,	specific heat [J/kg, K];
D_0,	change-in-phase detectability factor (reduced);
D_c,	critical detectability factor;
E,	total energy [J];
e,	energy per unit of mass [J/kg];
ε,	specific bond energy of cluster (per molecule) [J];
i, i', i'',	enthalpy, ... of liquid, ... of vapor [J/kg];
K,	universal fluid constant, $K = 6.765 \pm 0.015$;
K_0, K_1, K_2,	constants in equations;
k,	Boltzmann's constant, $k = 1.38 \cdot 10^{-23}$ [J/K];
M,	mass of fluid [kg];
m,	mass of elementary particle, $m = M/S$ [kg];
μ,	relative mass of cluster [u];
μ_0,	molecular mass [u];
N,	number of clusters;
N_s,	number of molecules in the surface layer of a nucleus;
n,	number of elementary particles per cluster;
n_s,	specific number of molecules (per unit of surface area);
v, v', v'',	clusteral mass, ... of liquid, ... of gas ($v = \mu/\mu_0$);
P,	pressure [N/m^2];
p,	instantaneous number of groups;
π,	reduced pressure, $\pi = P/P_c$;
R,	special function; gas constant, $R = R_0/\mu$ [J/K, kg];
R_0,	universal gas constant, $R_0 = 8315$ [J/K, kmol];
r,	change-in-phase energy, or, latent heat of vaporization [J/kg];
S,	number of elementary particles;
σ,	surface energy [J/m^2];
T,	absolute temperature [K];
τ,	reduced temperature, $\tau = T/T_c$;
τ_0,	triple point temperature (reduced);
U,	internal energy [J];
u,	specific internal energy [J/kg];
V,	volume [m^3];
v, v', v'',	specific volume, ... of liquid, ... of gas [m^3/kg];
w,	velocity of particle [m/s].

Subscripts

a,	average; corresponds to the average;
b,	bond energy;
c,	critical;
e,	elastic (or cohesive) energy;
k,	kinetic energy;
m,	maximum; corresponds to the maximum;
s,	saturation; corresponds to saturation.

1. CONCEPT OF CLUSTER

OWING to the existence of a field, fluid molecules group together in statistically defined clusters [1–5]. Considerable experimental evidence has also been collected on this effect [6–8].

In this paper, a cluster is described as follows. A given gas quantity having mass M, volume V and temperature T is made up of S elementary fluid particles, the mean mass of which $m = M/S$. The particles agglomerate into structures named clusters. All clusters consisting of n_i elementary fluid particles constitute a group of equal clusters. If N_i clusters make such a group, then the instantaneous number of elementary particles per group will be $S_i = N_i n_i$, where $i = 1, 2, 3, \ldots, p$; and p, the instantaneous number of groups. Thus, the instantaneous mean number of elementary particles per cluster amounts to:

$$\bar{n} = \sum_1^p N_i n_i \Big/ \sum_1^p N_i .$$

This definition is in agreement with the conclusion made by Buckle in his "kinetic energy theory of cluster formation" [5], where he attempts to calculate the course of homogeneous condensation in a classical monoatomic vapor from molecular rather than surface energy and other thermodynamic precepts.

As distinct from a cloud of non-interacting particles, the cluster is a structure with a center of attractive forces. So, the cluster is supposed to be a body. Therefore, in the proposed model, clusters are treated as point masses and by analogy with the kinetic theory of gases, as carriers of the translational kinetic energy component of total gas energy.* Consequently, the partial pressure P_i, which results from (N_i/V) clusters per unit of volume, will be:

$$P_i = (N_i/V)kT.$$

Since the specific volume $v = V/M$ and $M = m\sum_1^p N_i n_i$, the total pressure is given by

$$P = \sum_1^p P_i = (kT/v)\sum_1^p N_i \Big/ m\sum_1^p N_i n_i = (k/m)(1/n)(T/v).$$

If we assume that the mass of elementary particle $m = 1.66 \times 10^{-27}$ kg, then the ratio k/m becomes a universal gas constant, $R_0 = k/m = 8315$, and the equation of state of a real gas takes the following form:

$$Pv = (R_0/\mu)T = BT \tag{1}$$

where $\mu = n$, the mean relative mass of cluster (expressed in atomic mass units, u). This is the same equation as derived by Buckle [5].

So, unlike an ideal gas, the state of a real gas is defined by four parameters. For a number of technologically important fluids the function $B = B(P, v, T)$ is experimentally known (Saturated and Superheated Vapor Tables). Then equation (1) helps to directly determine the dependence of the mass of cluster on the parameters of state: $\mu = f(P, v, T)$.

A cluster, as a structure having a center of attractive forces, is qualified by its bond energy. Also, due to the existence of a field, there are attractive forces acting among the clusters (cohesive energy). It follows that the total energy of the mass M of a real gas can be considered as a sum of three components:

$$E = U_k - U_b - U_e = f(P, T, v, \mu) \tag{2}$$

where: U_k, kinetic energy of clusters; U_b, the bond energy of clusters; and U_e, the cohesive energy.

It is known that each susceptible energy form can be detected only by applying an appropriate device. However, some energy forms are not detectable, though their quantities are measurable indirectly.

In our case, temperature and pressure belong to the first group. They are normally detectable by means of a thermometer and a manometer, respectively. To the second group belong the bond and cohesive energies, and consequently, the total energy of gas.

The detection methods mentioned are based on the detection of kinetic energy of particles, i.e. constituents of the gas in question. Thus, it has been assumed here that only the first component of the total gas energy:

$$U_k = N\mu w^2/2 = (3/2)NkT = (3/2)PV \tag{3}$$

is detectable by means of a thermometer or manometer, while the remaining two energy components, U_b and U_e, are non-detectable. Thus, in order to correlate the parameters of state, P and T, with the total gas energy E, the following function, called detectability function, has been introduced:

$$D = \mathrm{d}E/\mathrm{d}U_k = \mathrm{d}e/\mathrm{d}u_k.$$

By combining this function with equation (2) we obtain:

$$\mathrm{d}e = D\,\mathrm{d}u_k = \mathrm{d}u_k + \mathrm{d}(u_b + u_e). \tag{4}$$

This is the foundation of the concept of detectability.

2. CHANGE-IN-PHASE DETECTABILITY FACTOR

The change-in-phase equilibrium state makes it possible to reduce the number of independent variables presented in equations (1) and (2). Let us consider a liquid changing into vapor at constant temperature and pressure, T_s and P_s. So, from equation (4), and with the subscript s indicating the change in phase state, it follows:

$$\mathrm{d}e_s = \mathrm{d}u_{ks} + \mathrm{d}(u_{bs} + u_{es}) = D_s\,\mathrm{d}u_{ks}.$$

As a matter of fact, in the equilibrium state considered here, the ratio $\mathrm{d}u_{ks}/\mathrm{d}(u_{bs} + u_{es})$ is small as compared to unity, so that we can write:

$$\mathrm{d}e_s = D_s\,\mathrm{d}u_{ks} \gtrsim \mathrm{d}(u_{bs} + u_{es}).$$

From equation (3), which reads $u_{ks} = (3/2)P_s v_s$, we have $\mathrm{d}u_{ks} = (3/2)P_s\,\mathrm{d}v_s$, followed by the integral:

$$\int_{e'}^{e''} \mathrm{d}e_s = \int_{e'}^{e''} D_s\,\mathrm{d}u_{ks} = (3/2)P_s\bar{D}_s \int_{v'}^{v''} \mathrm{d}v_s. \tag{5}$$

Bearing in mind that the following holds:

$$\int_{e'}^{e''} \mathrm{d}e_s = e'' - e' = r$$

and that, by definition, the latent heat of vaporization equals the difference in the enthalpies, i.e. $r = i'' - i'$, it follows:

$$\mathrm{d}e_s = \mathrm{d}i_s = \mathrm{d}(u_{bs} + u_{es}). \tag{6}$$

Finally, with $D_a = (3/2)\,\bar{D}_s$, we obtain, from equation (5), an expression for the average detectability factor:

$$D_a(\tau) = r/P_s(v'' - v'). \tag{7}$$

When τ approaches the critical point $(\tau \to 1)$, the expression $r/P_s(v'' - v')$ becomes undefinable. However, using the Saturation Vapor Tables, the D_a-values have been determined for a number of real fluids within the range of temperatures $\tau_0 < \tau < 1$, and plotted in a diagram, shown in Fig. 1. There have appeared two significant qualities of curves obtained in this way:

(1) The range of major scatter of measured points,

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*This means that other modes of kinetic energy, such as vibrational and rotational, have been formally neglected, but implicitly involved in bond energy.

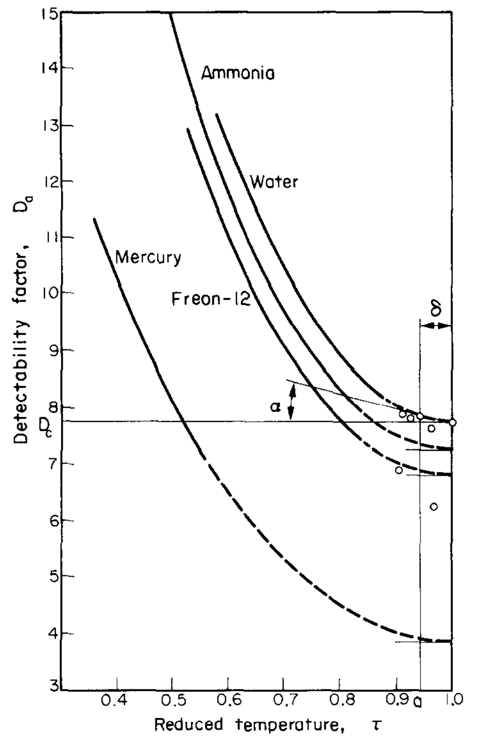

FIG. 1. Average detectability.

δ, is very narrow as compared to unity (0.05 and less); and

(2) The slope of curves under consideration at point *a*, tan α, is close to α.

Keeping these two things in mind, as well as a very smooth shape of the curves and their extreme mutual similarity, first, the existence of a function $D_a = f(\tau)$ has been assumed with a minimum at the point $\tau = 1$, that is $(df/d\tau) = 0$, and $f(\tau) = D_c$; and secondly, a reduced detectability function,

$$D_0(\tau) = D_a/D_c = f(\tau)/D_c \qquad (8)$$

has been defined by the following three statements:

(a) $d^2D_0/d\tau^2 = K/\tau \quad (K > 0, \text{constant})$
(b) $dD_0/d\tau = 0 \quad \text{at } \tau = 1$
(c) $D_0(\tau) = 1 \quad \text{at } \tau = 1.$

The solution of differential equation (a), with boundary conditions (b) and (c), gives an expression for the reduced detectability function, termed here the "change-in-phase detectability factor":

$$D_0 = 1 + K(\tau \ln \tau - \tau + 1). \qquad (9)$$

On the other hand, from equations (7) and (8) it follows:

$$D_0 = r/D_c P_s(v'' - v'). \qquad (10)$$

The D_c-values have been determined for a number of fluids [9] and then the equations (9) and (10) compared within the temperature range $\tau_0 < \tau < 1$, as shown in Table 1 and Fig. 2.

This results in the conclusion, interesting as much as practical, that *K* may be considered as a universal fluid constant whose value approximates $K = 6.765 \pm 0.015$, and consequently, the function $D_0(\tau)$ should be regarded as a universal law, expressed by equation (9).

Table 1. Critical detectability factor, D_c

Fluid	Chemical symbol	D_c
Water	H_2O	7.75
Mercury	Hg	4.00
Carbon dioxide	CO_2	7.00
Ammonia	NH_3	7.27
Freon-12	CF_2Cl_2	6.70
Freon-22	CHF_2Cl	7.16

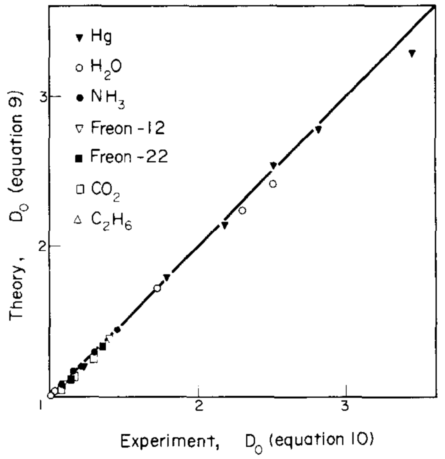

FIG. 2. Reduced detectability.

3. CLUSTERAL MASS IN A CHANGE-IN-PHASE STATE

Equation (1) is applicable to real fluids the molecular mass of which is μ_0. Thus, an expression for the number of molecules per cluster, termed clusteral mass, is directly obtained:

$$v = (R_0/\mu_0)(T/Pv) = (R_0 T_c/\mu_0 P_c)(\tau/\pi v). \qquad (11)$$

This gives an essentially different explanation, i.e. another physical meaning to the complex (RT/Pv), already known in thermodynamics as compressibility. The same expression was derived by Buckle [5].

In case the fluid is in a change-in-phase state, it is well known how the pressure π and the specific volumes of liquid and gaseous phases, v' and v'', depend on temperature. By means of these dependences clusteral masses can be calculated from equation (11).

Thus, clusteral masses v' and v'' have been determined for several fluids within the temperature range $\tau_0 < \tau < 1$ and plotted in a diagram, shown in Figs. 3 and 4.

As far as the function $\tau = f(v'')$ is concerned, one can see from this diagram that two wide temperature ranges are particularly characteristic: the initial range, in which single molecules (monomers) predominate; and the subsequent range, where clusters composed of two molecules each (dimers) come into being. Only in a comparatively narrow temperature range, δ, in the vicinity of the critical point, larger clusters (trimers and quadrimers) are predominant. In this narrow range, the curve approaches a point $v'' = v_c$, where $d\tau/dv'' = 0$ and $\tau = 1$. Similarly, the function $\tau = f(v')$, after passing a singular point, suddenly reaches the point $v' = v_c$, where $d\tau/dv' = 0$ and $\tau = 1$ (Fig. 5).

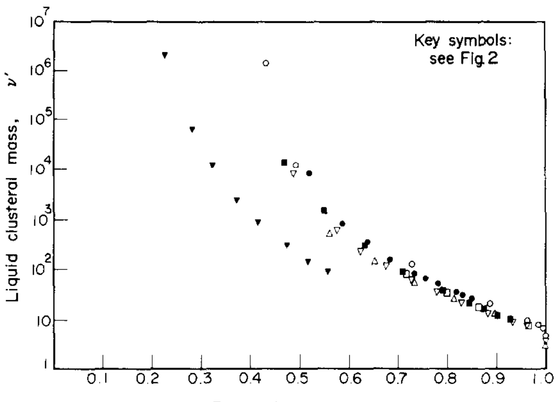

FIG. 3. Variation of liquid clusteral mass with saturation temperature.

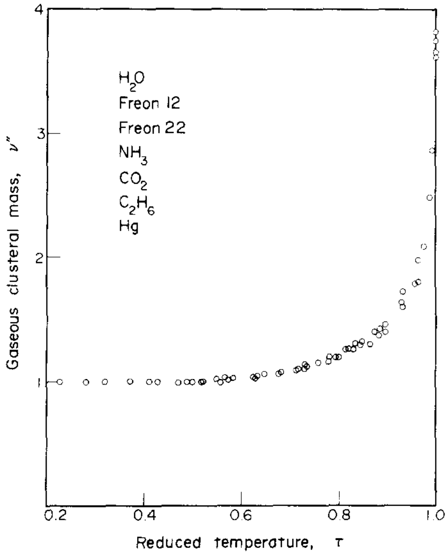

FIG. 4. Variation of gaseous clusteral mass with saturation temperature.

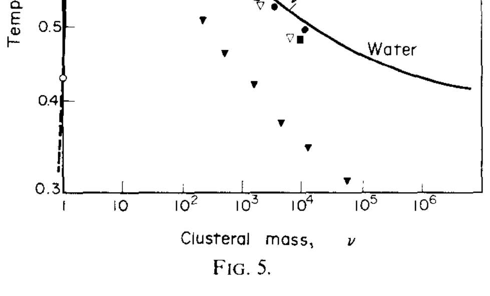

FIG. 5.

These curves can be very successfully approximated by the following two expressions (up to the point $\tau = 1-\delta \approx 0.97 \pm 0.01$):

$$\nu' = 10\exp[K_1(1-\tau)/\tau] \tag{12}$$

and

$$\nu'' = [(a-\tau_0)/(a-\tau)]^K \tag{13}$$

where:

$$K_1 \ldots K_2, \text{ fluid constants;}$$
$$a = (\tau_0 - \nu_c^{1/K})/(1-\nu_c^{1/K});$$
$$\nu_c = 4.0 \pm 0.25.$$

4. ENTHALPY OF VAPOR AS A FUNCTION OF SATURATION TEMPERATURE

In order to demonstrate the usefulness of the newly introduced concept of detectability, an attempt has been made in the following two sections to derive the function $i'' = f(\tau)$, and the equation of phase equilibrium, $\pi = f(\tau)$.

Equation (4) may assume the form: $(D-1)\,\mathrm{d}u_k = \mathrm{d}(u_b + u_e)$ which, for saturated vapor and using equation (9), reads:

$$D_c[D_0(\tau)-1]\,\mathrm{d}u_k'' = \mathrm{d}(u_b'' + u_e'').$$

Bearing in mind equation (6), the above expression becomes:

$$\mathrm{d}i'' = D_c[D_0(\tau)-1]\,\mathrm{d}u_k''. \tag{14}$$

However, if applied to clusters of saturated vapor, equation (3) may be written as follows:

$$\begin{aligned} u_k'' &= (3kT_c/2M)N\tau \\ &= (3kT_c/2\mu_0)(\tau/\nu'') \\ &= (1/2K_0)(\tau/\nu'') \end{aligned}$$

where: $K_0 = \mu_0/3kT_c$;

Using the differential of the last expression, which reads

$$\mathrm{d}u_k'' = (1/2K_0)(\tau/\nu'')(\mathrm{d}\tau/\tau - \mathrm{d}\nu''/\nu''),$$

and equation (9) being substituted for D_0, equation (14) assumes the following form:

$$(2K_0/D_cK)\,\mathrm{d}i'' = (\tau\ln\tau - \tau + 1)(\tau/\nu'')(\mathrm{d}\tau/\tau - \mathrm{d}\nu''/\nu''). \tag{15}$$

Now, with equation (13) and (15) it is possible to derive an expression showing a relationship between enthalpy and saturation temperature, though in a differential form. Finally an integration (numerical or graphical) of this relation enables to obtain enthalpy i'' as function of τ, up to the constant of integration.

5. EQUATION OF PHASE EQUILIBRIUM

By comparing equation (10) with the well-known Clausius–Clapeyron equation:

$$\mathrm{d}P/\mathrm{d}T = r/T(v''-v')$$

we can directly obtain the differential equation of phase equilibrium:

$$\mathrm{d}\pi/\mathrm{d}\tau = D_cD_0(\tau)\pi/\tau.$$

To solve it equation (9) has been used and after rearrangement the equation of phase equilibrium is obtained in its general form:

$$\ln\pi = D_c\ln R \tag{16}$$

where

$$\ln R = [1+K(1+\tau)]\ln\tau + 2K(1-\tau).$$

Bearing in mind that $K = \text{const.}$, as shown in Section 2, the function $\ln R$ may be tabulated for convenience once and for all.

The equation of phase equilibrium (equation 16) is checked for correctness [9]. Applying this equation to a number of fluids, pressure values are calculated for the range of points $\tau_0 < \tau < 1$ and then deviations from the tabular values obtained. It has been shown, for the fluids examined, that the deviations are mostly about $\pm 0.2\%$, increasing only in the vicinity of triple and critical points. Namely, near the critical point, they go up to $+1.5$, and near the triple point, up to $+5\%$.

6. VAPORIZATION AND LIMITING LIQUID SUPERHEAT

A liquid vaporizes either in its volume by forming bubbles, or, without bubbling, from its free surface. The former case is called *boiling*, while the latter is known as *free surface vaporization*. This paper considers the so-called undisturbed pool boiling. The starting assumption is that in a system under consideration the mean pressure does not change during the boiling.

Boiling which occurs after isoentropical depressurization of a liquid in which there is no heating surface, is called *volume boiling*. The distribution of vapor bubbles formed in the liquid volume is quite casual. The liquid at pressure P_s and saturation temperature T_s becomes, after depressurization ΔP, evenly superheated with relation to the lowered pressure $P' = P_s - \Delta P$. This condition is termed metastable equilibrium, or metastable liquid superheat.

When liquid borders on a heating surface, the vapor bubbles appear on this surface. The phenomenon is termed *surface boiling*. The heating surface and the comparatively thin liquid layer next to it are at temperatures higher than the respective saturation temperature. Accordingly, the liquid in this boundary zone is always superheated, while the temperature outside this zone may be either equal or subcooled compared to the saturation temperature. Thus, there are two different conditions under which the phenomenon can take place, and therefrom the terms: *saturation boiling* and *subcooled boiling*.

In accordance with the accepted model, liquid is made up of clusters. A cluster may be regarded as a microscopic drop differing from a macroscopic drop not only in size (Frenkel [3]), but also in that it is composed of individual molecules, while a macroscopic drop consists of molecule clusters. When colliding with another cluster or with some other solid body, the resulting structure reaches an excited internal state that may be high enough to cause the partial destruction (splitting), or total destruction (vaporization) of the structure. For a given expenditure of kinetic energy, the cluster reaches a maximum excitation only in central inelastic collision with a large solid body, or with a similar cluster moving at the same velocity but in the opposite direction.

Imagine an infinite liquid continuum under pressure P_s and at saturation temperature T_s. Let's assume a small volume having mass M, whose excitation has been increased by an amount $M\,\mathrm{d}e$. Suppose that the specific energy of critical excitation, Δe, is sufficient to convert a liquid unit mass into a vapor bubble having volume v''. Then we have $M = Sm = V/v''$ and the energy balances will be:

$$M\Delta e = M\int_L^V \mathrm{d}e = M\int_L^V \mathrm{d}i + \int_L^V \mathrm{d}E_T$$
$$= M(i''-i') + Mc\Delta T$$

and

$$M\Delta e = \int_{\varepsilon'}^{\varepsilon''} \mathrm{d}(S\varepsilon) + MP_s\int_{v'}^{v''} \mathrm{d}v + \sigma\int_0^A \mathrm{d}A$$

where: $\mathrm{d}E_T = Mc\,\mathrm{d}T$, energy of metastable superheat; ε, bond energy of cluster per molecule; σ, specific bond energy of liquid's surface structure, also called surface energy; A, surface area of a bubble.

The above two balances indicate, firstly, that the total energy $M\Delta e$ appears in two forms, i.e. as a change in enthalpy and as a liquid superheat. Secondly, during the formation of a bubble this energy is transformed into: (a) a change in bond energy (the transition from liquid to vapor clusters); (b) work done by vapor expansion; and (c) the bubble surface energy.

Upon integration we have,

$$\Delta e = i''-i'+c\Delta T = (\varepsilon''-\varepsilon')/m + P_s(v''-v') + Av''\sigma/V.$$

Considering that $i''-i' = r = u''-u'+P_s(v''-v')$, it is finally possible to write down:

$$c\Delta T = Av''\sigma/V + (\varepsilon''-\varepsilon')/m - (u''-u'). \tag{17}$$

The bubble volume V may take an arbitrary shape. However, only the form of a sphere is a stable structure, considering that for a bubble having a given volume V_c the ratio V_c/A reaches its maximum when the volume assumes a spherical shape:

$$V_c/A_{\min} = (V_c/A)_{\max} = \rho_c/3 \tag{18}$$

where ρ_c is radius of the spherical bubble.

A minimum spherical bubble is called a *nucleus*. Suppose that a nucleus originates from a microscopic liquid mass consisting of v_c molecules; then the radius of the nucleus will be,

$$\rho = (3v''mv_c/4\pi)^{1/3}. \tag{19}$$

It follows from (18) and (19),

$$A_{\min}/V_c = 3/\rho_c = (36\pi)^{1/3}(v''mv_c)^{-1/3}$$

which, when substituted in (17), gives the following expression for the limiting metastable liquid superheat ΔT:

$$c\Delta T = (36\pi)^{1/3}v''^{2/3}(mv_c)^{-1/3}\sigma$$
$$+ (\varepsilon''-\varepsilon')/m - (u''-u'). \tag{20}$$

It is important to note that the physical nature of specific energies σ and ε is identical, and therefore there must be an analytical relationship between them. If we knew the number of molecules N_s composing the *surface layer* of liquid surrounding the nucleus then, knowing the size of the nucleus, we could easily find out the density of molecules in the layer: $n_s = N_s/A_c$, wherefrom the required relationship would follow:

$$\sigma = n_s \varepsilon. \tag{21}$$

Upon coming into a central collision, a drop of mass mv_c is deformed into a flat circular disk. With sufficient excitation, this deformation may finish in the decomposition of the disk into individual monomers (molecules) and comparatively few dimers and trimers. The surplus of excitation energy appears as the kinetic energy of these particles. In other words, there arises a gaseous substance that is commonly termed vapor. While expanded, the vapor forms an unstable lenticular cavitation, but if it possesses critical energy, it will form a stable spherical nucleus. By means of equation (19) it is thus possible to obtain the surface area of the nucleus:

$$A_c = 4\pi(3v''mv_c/4\pi)^{2/3}. \tag{22}$$

At critical excitation, the drop will be maximally stretched into a monomolecular layer the surface of which may be either flat or curved. If flat, the nucleation will begin with a lenticular shape. This means that in the surface layer of such a cavitation there will be at least $2v_c$ molecules, or more, which is deduced from purely geometrical reasoning. If, however, the stretch surface is curved, this number will be smaller. On this basis, the number of molecules in the surface layer is given by the expression, $N_s = xv_c$, where $x \geqslant 2$. In this way, by means of $n_s = N_s/A_c$ and using equation (22), we get,

$$x = n_s(36\pi/v_c)^{1/3}(mv'')^{2/3}. \tag{23}$$

It follows from (21) that the density of molecules in the surface layer, n_s, is determined by the physical nature and thermodynamic condition of the fluid, considering that for each fluid there are definite dependences, $\sigma(T)$ and $\varepsilon(T)$. Keeping equation (23) in mind, it follows that the quantity x must also be a function of the same parameters. The difficulty is in that the function $\sigma(T)$ is known for some fluids, while the corresponding function $\varepsilon(T)$ is not. It is, however, possible to assert *a priori* that $\varepsilon = 0$ for $v = 1$. Thus, as long as $v'' \approx 1$, we can take it that $\varepsilon'' \approx 0$ as well; consequently, making use of (23), we obtain from equation (20):

$$c\Delta T = \left(1 - \frac{1}{x}\right)(36\pi v''^2/mv_c)^{1/3}\sigma - (u'' - u'). \tag{24}$$

Namely, this equation is valid in the range of relatively small temperatures only.

So far, we have seen that the parameter $(x \geqslant 2)$ depends on the kind of fluid and the temperature. An additional conclusion is now derived from equation (24), saying that the lower limit of x is given by the expression: $1/x < F$, where

$$F = 1 - (\Delta u/\sigma)(36\pi v''^2/mv_c)^{-1/3}.$$

We are easily assured by a numerical check that in the real domain F is slightly smaller than unity. For water, indeed, $x = 1.4\ldots4$, within the range of $\tau = 0.422\ldots0.55$.

To be able to apply expression (24) to surface boiling, we must remember that we are dealing here with continual transfer of energy through a heating surface. The difference between the heating surface temperature and the mean temperature of the thin boundary layer is given by the well-known relationship:

$$\Delta T_w = q/\alpha$$

where q, thermal flux through the heating surface, and α, heat-transfer coefficient.

In this way, equation (24) is obtained in a form adjusted to the parameters of surface boiling:

$$c\Delta T_w = cq/\alpha = 4.836\sigma(v''^2/mv_c)^{1/3}(1 - 1/x) - \Delta u. \tag{25}$$

The thin boundary layer mentioned above may be considered as a uniformly superheated zone in which the nucleation and the initial growth of a bubble take place, while the remaining part of the volume practically plays no role in this process. Consequently, ΔT_w is not dependent on whether the saturation or subcooled boiling takes place, which is in agreement with experimental evidence [10].

In addition, equation (25) shows that, under given conditions, the thermal flux q can be changed within a wide range without any apparent effect on ΔT_w, provided there is a simultaneous reciprocal change in the coefficient α. This was also experimentally confirmed by Stefanović [10].

The heating surface exerts a decisive influence on the number of molecules N_s which go to form the surface layer of a nucleus. Namely, when colliding with the heating surface, the cluster is stretched into a monomolecular layer which for a moment sticks to the heating surface due to adhesion. Just thereafter, owing to some additional impulses from the heating surface, the molecular layer disintegrates and the free molecules form a semilenticular bubble. The size of the bubble base, which is part of the heating surface, obviously depends on the wetting angle. Furthermore, geometrically speaking, it is evident that, when a cluster collides with heating surface and for a given v_c, the quantity $x = N_s/v_c$ is minimal compared to all other kinds of nucleation considered here. However, in equation (25) for a minimum x the coefficient $(1 - 1/x)$ will be minimal. This easily accounts for the well-known experimental fact about the great difference in the degree of superheat between volume and surface boiling. It is worth mentioning that until now this phenomenon has not been explained at all [10].

Likewise, the initial shape of the stretched molecular layer may be considerably affected by impurity particles contained in the liquid, and even by the microgeometry of the heating surface, although definitely not in the domain of crevice size where Bankoff [11] tried to find an explanation for this effect. In this connection Novaković [12] has already asserted his doubt based on the well known experiments of water boiling on the mercury heating surface. Phenomenologically, the influence of the above factors is well known, but it is only on the basis of the mechanism described here that it becomes clear that attempts to interpret analytically all possible influences on which metastable superheat depends in real conditions are next to hopeless.

Unlike the lenticular bubble, which easily yields to external pressure and collapses, the spherical nucleus may survive in the conditions of natural fluctuations of liquid density. The moment that the nucleus comes into being, the surrounding temperature T_L may be the same as, lower or higher than the nucleus temperature, T_s. If $T_L > T_s$, then under the action of free surface vaporization, the nucleus begins to grow without changing its spherical shape. The bubble growth is a well studied phenomenon, especially when volume boiling is meant. This growth will last as long as the energy is transferred from the surroundings towards the cavitation surface.

While the bubble's diameter is increased, the strength of the surface layer is gradually decreased, so that the fluctuations and convective movement of liquid begin to deform it more easily. Furthermore, the coalescence of bubbles becomes more frequent as they come upon each other.

The reduced limiting superheat, as given by equations (24) and (25) has been compared with the experimental results [13–15] in the domain of their validity. The agreement of the theory with the experiments is almost perfect.

7. CONCLUSION

The proposed model of fluid enables us to acquire a better understanding of liquid's behaviour during the process of vaporization. It also proves to be a useful instrument for calculating the corresponding fluid parameters with a fairly high accuracy.

The statement that the mass of a complex fluid particle, a cluster, should not be considered as constant but rather as dependent on the parameters of state, seems to be fully justified.

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CHANGEMENT DE PHASE D'UN FLUIDE CONSTITUE D'AGREGATS MOLECULAIRES

Résumé—Dans le présent aeticle l'existence d'agrégats moléculaires est supposée *a priori*. On montre que la masse statistique moyenne d'un agrégat dépend des variables d'état du gaz, tandis que l'énergie cinétique moyenne des agrégats est proportionnelle à la température mesurée et l'énergie cinétique volumique proportionnelle à la pression mesurée.

Le concept de détection de la température et de la pression a été introduit et on a obtenu une expression pour le facteur de détection en changement de phase. De plus, on a obtenu des expressions pour la pression de saturation et pour le nombre moyen de molécules par agrégat en fonction de la température de saturation.

Enfin, un modèle de vaporisation est proposé duquel on déduit une expression de la surchauffe limite du liquide.

L'accord de ces expressions avec les résultats expérimentaux s'avère presque parfait.

DER PHASENWECHSEL EINES AUS MOLEKÜL-CLUSTERN ZUSAMMENGESETZT BETRACHTETEN FLUIDES

Zusammenfassung—In der vorliegenden Arbeit wird das Vorhandensein von Molekül-Clustern a priori angenommen; es wird gezeigt, daß die mittlere statistische Masse eines Clusters von den Gaszustandsgrößen abhängt, während die mittlere kinetische Energie der Cluster proportional zur gemessenen Temperatur und die auf die Volumeneinheit bezogene kinetische Energie proportional zum gemessenen Druck ist. Es wurde das Konzept der Trennbarkeit von Temperatur und Druck eingeführt und ein Ausdruck für den Phasenwechsel-Trennfaktor abgeleitet. Zusätzlich wurde ein Ausdruck für den

Sättigungsdruck und die mittlere Molekülzahl pro Cluster als Funktion der Sättigungstemperatur abgeleitet. Schließlich wurde ein Verdampfungsmodell vorgeschlagen und eine Beziehung für die Grenzüberhitzung der Flüssigkeit hergeleitet. Die Übereinstimmung all dieser Beziehungen mit den experimentell ermittelten Werten ist nahezu vollkommen.

ФАЗОВОЕ ПРЕВРАЩЕНИЕ ГАЗА, СОСТОЯЩЕГО ИЗ МОЛЕКУЛЯРНЫХ КЛАСТЕРОВ

Аннотация — В статье существование молекулярных кластеров принимается *a priori*, что показывает, что средняя статистическая масса отдельного кластера зависит от параметров состояния газа, тогда как средняя кинетическая энергия кластеров пропорциональна измеренной температуре, а кинетическая энергия на единицу объема — измеренному давлению газа. Введены понятия температуры и давления и получено выражение для коэффициента определяемости фазового превращения. Кроме того, получены выражения для давления насыщения и среднего числа молекул в кластере как функций температуры насыщения. Наконец, предложена модель парообразования и получено выражение для предельного перегрева жидкости. Согласие полученных выражений с экспериментальными данными оказалось почти идеальным.