

CONCERNING THE NUMBER OF CONDENSATION CENTERS

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It is shown that for rapid adiabatic expansion processes a considerable contribution to the rate of formation of condensation centers is made by the mobility of the boundary between stable drops and droplets of subcritical size formed as a result of heterophase fluctuations.

Modern ideas concerning the condensation mechanism [1-3] associated with the adiabatic expansion of a superheated and saturated vapor can be expressed in the following very condensed form.

In the superheated and saturated vapor there are heterophase fluctuations that lead to the formation of droplets of liquid phase. The number of these droplets\* diminishes very quickly as their diameter (the number of molecules in the droplet) increases. This number can be determined from the formula

$$N(g) = C \exp\left(-\frac{\Delta\varphi g + bg^{2/3}}{kT}\right). \quad (1)$$

For the superheated and saturated vapor the quantity  $N(g)$  is a monotonically decreasing function depending on  $g$ , since in this case  $\varphi_B > \varphi_A$  and hence  $\Delta\varphi > 0$ .

In the case of a supercooled vapor the quantity  $N(g)$  has a distinctly expressed minimum, since for the supercooled vapor  $\varphi_B < \varphi_A$  and hence  $\Delta\varphi < 0$ .

It is easy to show that this minimum is observed when

$$\frac{2}{3} bg_{cr}^{2/3} - (\varphi_A - \varphi_B) g_{cr} = 0.$$

In this case

$$N(g_{cr}) = C \exp\left[-\frac{(\varphi_A - \varphi_B) g_{cr}}{2kT}\right]. \quad (2)$$

When  $g > g_{cr}$  the number of droplets begins to increase.

Thus, in the region of superheated vapor and at  $g < g_{cr}$  the distribution  $N(g)$  is purely dynamic; the drops are unstable. At  $g > g_{cr}$  the drops are stable; they do not disintegrate but become condensation centers. As condensation proceeds, the number of molecules in the drop increases and, consequently, so does its stability.

We note that the quantity  $N(g)$  is a stationary distribution, i. e., the distribution that exists in a system in the equilibrium state. In this sense  $N(g)$  is a category characteristic only of a superheated and saturated vapor. A supercooled vapor, by its very nature, cannot be in the equilibrium state, i. e., in a supercooled vapor a stationary distribution  $N(g)$  cannot be achieved; in the supercooled vapor a process occurs in which a certain number of droplets pass

through the critical size and form condensation centers. This process continues until the supercooled vapor goes over into the state of dry saturated vapor and liquid droplets.

The rate of formation of condensation centers can be obtained on the assumption that the liquid droplets formed are eliminated from the system and replaced by the same number of individual molecules. As a consequence, a certain stationary droplet distribution (different from the  $N(g)$  distribution) and a certain droplet flux through the critical diameter develop in the supercooled vapor.

The number of condensation centers (the droplet flux through the critical diameter per unit time, the rate of formation of condensation centers) is then determined from the formula

$$I = 2r_{cr}^2 \frac{p}{kT} \sqrt{\frac{(\varphi_A - \varphi_B)}{3m}} g_{cr} \exp\left(-4\pi \frac{\sigma r_{cr}^2}{3kT}\right). \quad (3)$$

Here,  $r_{cr}$  is the critical radius:

$$r_{cr} = \frac{2\sigma v_B}{\varphi_A - \varphi_B}.$$

In the process of adiabatic expansion in Laval nozzles the flow is supercooled [4], and the amount of condensed moisture is determined from the formula proposed by Oswatich [5]:

$$Y(l) = \frac{1}{G} \int_{l_0}^l m(l', l) I(l') F(l') dl'. \quad (4)$$

Here,  $m(l', l)$  is the mass of a drop formed in section  $l'$  after it reaches a section  $l$ ; to a considerable extent it is determined by the rate of growth of the drop;  $I(l')$  is the rate of formation of condensation centers in section  $l'$ ;  $F(l')$  is the cross-sectional area; and  $l_0$  the coordinate of the section in which the flow intersects the upper boundary curve.

Examples of the numerical solution of the problem of vapor flow in nozzles based on the above ideas can be found in [6, 7]. In most cases the agreement between theory and experiment is satisfactory. Nonetheless, in our view, the above method of determining the number of condensation centers disregards certain important factors. This applies particularly to rapid processes of adiabatic expansion.

\*For brevity, the term "droplet" is used for particles of subcritical diameter.

In these processes, apart from the condensation centers that result from the addition of molecules and the consequent increase in the diameter of the drops to the critical value and above, new condensation centers appear as a result of the fact that the critical size decreases in the process of adiabatic expansion. In other words, the total number of condensation centers is composed both of droplets that have crossed the critical diameter in the process of heterophase fluctuation and droplets of the preexisting distribution, owing to the decrease in the critical diameter during adiabatic expansion. For example, in the case of a process of infinitely rapid adiabatic expansion the number of condensation centers due to droplet growth will be equal to zero, whereas the number of condensation centers due to the sharp decrease in critical diameter will be very considerable. This explains why supercooling in excess of 60–70° K cannot be achieved even in the case of very rapid expansion. Clearly, if the expansion is very rapid, droplets already existing in the initial stationary distribution  $N(g)$  occupy the zone  $g > g_{cr}$ , and it is precisely these droplets that become condensation centers. Thus, owing to the mobility of the boundary between the stable and unstable drops new condensation centers appear, the total number of which can be defined as

$$n = \int_{g_{cr}}^{\infty} f(g) dg.$$

This quantity differs from  $N(g)$  in that  $N(g)$  is a stationary distribution, whereas  $f(g)$  corresponds to a non-equilibrium distribution.

In expansion processes that proceed at a finite rate it is possible to determine the flux of condensation centers (rate of formation of new condensation centers) due to the mobility of the boundary between stable and unstable drops as follows:

$$I' = -f(g) \frac{dg_{cr}}{d\tau} = f(g) \frac{dg_{cr}}{d\Delta T} \frac{d\Delta T}{dp} \frac{dp}{dl} \frac{dl}{d\tau}.$$

Keeping in mind that  $dl/d\tau = u$  is the flow velocity, we can rewrite the latter relation in the form

$$I' = uf(g) \frac{dg_{cr}}{d\Delta T} \left( \frac{dT_s}{dp} - \frac{dT}{dp} \right) \frac{dp}{dl}. \quad (5)$$

We evaluate one by one all the derivatives entering into this expression.

1. In determining  $dg_{cr}/d\Delta T$  two variants are possible.

a) When the supercooling is relatively small. In this case it is possible to use the familiar formula [1]

$$\frac{\Delta T}{T_s} = \frac{2\sigma v_B}{\lambda r_{cr}} \quad \text{or} \quad r_{cr} = \frac{2\sigma v_B T_s}{\lambda \Delta T}.$$

From this expression we easily find that

$$\frac{dr_{cr}}{d\Delta T} = -\frac{2\sigma v_B T_s}{\lambda \Delta T^2} = -\frac{\lambda}{2\sigma v_B T_s} r_{cr}^2. \quad (6)$$

But

$$\frac{dg_{cr}}{d\Delta T} = \frac{4\pi r_{cr}^2}{v_B} \frac{dr_{cr}}{d\Delta T}.$$

Using (6), we obtain

$$\frac{dg_{cr}}{d\Delta T} = \frac{8\pi\sigma r_{cr}^2}{\lambda} \frac{T_s}{\Delta T^2} = -\frac{32\pi\sigma^3 v_B^2 T_s^3}{\lambda^3 \Delta T^4}. \quad (6')$$

Using Avogadro's number ( $N_A = 6.0228 \cdot 10^{26}$ ) we can reduce formula (6') to a form convenient for practical calculations:

$$\frac{dg_{cr}}{d\Delta T} = -\frac{32\pi \cdot 10^{-6} \sigma^3 N_A}{r^3 \mu} \frac{T_s^3}{\Delta T^4}. \quad (7)$$

Here, it has been assumed that  $v_B N_A / \mu = 0.001 \text{ m}^2/\text{kg}$  (working medium—steam);  $\bar{r} = \lambda N_A / \mu$  is the latent heat of vaporization.

b) When the supercooling is relatively large. In this case it is possible to use the most general formula [1]

$$\ln \frac{T_s}{T} = \frac{2\sigma v_B}{\lambda r_{cr}} \quad \text{or} \quad r_{cr} = \frac{2\sigma v_B}{\lambda \ln \frac{T_s}{T_s - \Delta T}}.$$

From the latter expression we easily find that

$$\begin{aligned} \frac{dr_{cr}}{d\Delta T} &= -\frac{2\sigma v_B}{\lambda \left( \ln \frac{T_s}{T_s - \Delta T} \right)^2 (T_s - \Delta T)} = \\ &= \frac{\lambda}{2\sigma v_B (T_s - \Delta T)} r_{cr}^2. \end{aligned} \quad (8)$$

As before, we can write

$$\frac{dg_{cr}}{d\Delta T} = \frac{4\pi r_{cr}^2}{v_B} \frac{dr_{cr}}{d\Delta T}$$

or, using (8), obtain

$$\begin{aligned} \frac{dg_{cr}}{d\Delta T} &= -\frac{2\pi\lambda r_{cr}^4}{\sigma v_B^2 (T_s - \Delta T)} = \\ &= -\frac{32\pi\sigma^3 v_B^2}{\lambda^3 (T_s - \Delta T)} \left( \ln \frac{T_s}{T_s - \Delta T} \right)^{-4}. \end{aligned}$$

Finally, as for (7), we can write

$$\frac{dg_{cr}}{d\Delta T} = \frac{32\pi\sigma^3 10^{-6} N_A}{r^3 \mu (T_s - \Delta T)} \left( \ln \frac{T_s}{T_s - \Delta T} \right)^{-4}.$$

2. Along the phase transition line the derivative  $dT_s/dp$  is determined by the Clapeyron-Clausius equation

$$\frac{dT_s}{dp} = \frac{(v_A - v_B) T}{\lambda} = \frac{(v'' - v') T}{r}. \quad (9)$$

For the region of small pressures, where the volume of the liquid phase is small as compared with the volume of the vapor phase and as the equation of state of the saturated vapor we can use the equation of state of a perfect gas  $pv = RT$ , we obtain

$$\frac{dT_s}{dp} = \frac{RT^2}{rp}. \quad (9')$$

3. The derivative  $dT/dp$  for expansion with total supercooling is determined by the equation of the adiabatic curve, according to which

$$\frac{T^\kappa}{p^{\kappa-1}} = \text{const.}$$

The latter relation and Eq. (9) make it possible to obtain for the low-pressure region

$$\frac{d\Delta T}{dp} = \frac{dT_s}{dp} - \frac{dT}{dp} = -\frac{\kappa-1}{\kappa} \frac{T}{p} \left(1 - \frac{\kappa}{\kappa-1} \frac{RT}{r}\right).$$

In this expression the minus sign reflects the known fact that as the pressure decreases (flow accelerates) the supercooling increases.

4. Finally, the derivative  $dp/dl$  can be found from the well-known equation of gasdynamics (8) for a one-dimensional flow, when only the geometric factor is involved:

$$(M^2 - 1) \frac{du}{u} = \frac{dF}{F}. \quad (10)$$

Using the fact that, in accordance with the momentum equation

$$dp = -\rho u du,$$

we can rewrite Eq. (10) in the form

$$\frac{dp}{dl} = -\frac{\rho u^2}{(1-M^2)F} \frac{dF}{dl}.$$

Thus, for the region of comparatively low pressure, using the expressions obtained for the derivatives, we can write

$$I' = -32\pi u^3 \frac{\kappa-1}{\kappa} R \left(1 - \frac{\kappa}{\kappa-1} \frac{RT}{r}\right) \times \frac{f(g)}{1-M^2} \left(\frac{\sigma}{r}\right)^3 N_A \cdot 10^{-6} \frac{T_s}{\Delta T^4} \frac{1}{\mu F} \frac{dF}{dl}. \quad (11)$$

If the supercooling is considerable, the corresponding formula will be

$$I' = -32\pi \frac{\kappa-1}{\kappa} R \left(1 - \frac{\kappa}{\kappa-1} \frac{RT}{r}\right) \frac{u^3 f(g)}{F(1-M^2)} \times \left(\frac{\sigma}{r}\right)^3 N_A \cdot 10^{-6} \left(\ln \frac{T_s}{T_s - \Delta T}\right)^{-4} \frac{1}{T_s - \Delta T} \frac{dF}{dl}. \quad (12)$$

There are two possible methods of evaluating the quantity  $I'$ :

1. In the first variant we calculate the distribution of all the parameters along the nozzle and then determine  $I'$  from (11) or (12) depending on the supercooling.

2. In this variant the preparatory work is the same as before, the calculations including the construction of the supercooling distribution along the nozzle. The subsequent calculation of  $I'$  is based on the obvious equation

$$I' = f(g) u \frac{dg_{cr}}{d\Delta T} \frac{d\Delta T}{dl} = 32\pi u f(g) \left(\frac{\sigma}{r}\right)^3 \frac{N_A}{\mu} 10^{-6} \frac{T_s^3}{\Delta T} \frac{d\Delta T}{dl}.$$

The derivative  $d\Delta T/dl$  can be evaluated graphically. In the case of considerable supercooling we have

$$I' = 32\pi \left(\frac{\sigma}{r}\right)^3 \frac{N_A \cdot 10^{-6}}{\mu (T_s - \Delta T)} \times u f(g) \left(\ln \frac{T_s}{T_s - \Delta T}\right)^{-4} \frac{d\Delta T}{dl}.$$

It should be noted that  $I$  and  $I'$ , and hence their roles in the general process of formation of condensation centers, are essentially different. In the case of rapid expansion processes the role of  $I'$  is decisive. Conversely, in the case of slow expansion processes greater importance attaches to the increase in the number of condensation centers due to the fact that as a result of heterophase fluctuations a certain number of droplets "overstep" the critical diameter.

The number of droplets passing in unit time from class  $g$  to the class of particles with number of molecules  $g+1$  is determined from the differential equation [1]

$$I = -s(g) \beta N(g) \frac{\partial Z}{\partial g}, \quad (13)$$

where  $\beta$  is a coefficient representing the number of vapor molecules condensing per unit time per unit area. This coefficient does not depend on  $g$  and can be taken equal to the number of gas molecules per unit time per unit area, i. e., in the first approximation

$$\beta = \frac{p}{\sqrt{2\pi mkT}}.$$

The quantity  $Z = f(g)/N(g)$  entering into (13) represents the relation between the number of droplets of a given size actually existing in the vapor and the number of droplets in the equilibrium state. The quantity  $N(g)$  is given by Eq. (1).

Thus, the relation between the number of condensation centers of different origin is given by the obvious equation

$$\frac{I}{I'} = \frac{\beta f(g) \mu \Delta T^4}{32\pi \left(\frac{\sigma}{r}\right)^3 N_A \cdot 10^{-6} T_s \frac{d\Delta T}{dl}} \frac{\partial}{\partial g} \ln \frac{1}{Z}.$$

After a series of transformations we can reduce this relation to the form

$$\frac{I}{I'} = \frac{p \Delta T T_s}{2(2\pi RT)^{\frac{1}{2}} u \frac{\sigma}{r} \frac{d\Delta T}{dl}} \frac{\partial}{\partial g} \ln \frac{1}{Z}. \quad (14)$$

In obtaining the starting relation we used the fact that the droplet fluxes are calculated in the region of

the critical point, where

$$s(g) = 4\pi r_{cr}^2 = 16\pi \cdot 10^{-6} \left( \frac{\sigma}{r} \frac{T_s}{\Delta T} \right)^2.$$

An equation analogous to relation (14) above can be obtained for the case of considerable supercooling. In this case it should be taken into account that

$$s(g) = 16\pi \cdot 10^{-6} \left( \frac{\sigma}{r} \right)^3 \left( \ln \frac{T_s}{T_s - \Delta T} \right)^{-2}.$$

Consequently,

$$\frac{I}{I'} = \frac{\rho(T_s - \Delta T) \left( \ln \frac{T_s}{T_s - \Delta T} \right)^2}{2(2\pi RT)^{\frac{1}{2}} u \frac{\sigma}{r} \frac{d\Delta T}{dl}} \frac{\partial}{\partial g} \ln \frac{1}{Z}.$$

Thus, the problem reduces to the determination of the quantity  $Z$ . However, this is a question of independent interest.

The quantity  $Z$  can be estimated on the basis of the following considerations. In the case of relatively rapid adiabatic expansion the distribution  $N(g, 0)$  is preserved for a comparatively long time. Thus, in this case as the first approximation we can assume that in the process of expansion the initial distribution, determined by the initial parameters, is retained, i. e.,

$$Z = \frac{f(g)}{N(g)} \approx \frac{N(g, 0)}{N(g, \tau)} \approx \exp \left[ - \frac{(\Delta\varphi_i + \Delta\varphi_f)g}{kT_s} \right].$$

Consequently,

$$\frac{\partial}{\partial g} \ln \frac{1}{Z} = \frac{\Delta\varphi_i + \Delta\varphi_f}{kT_s}.$$

For example, for the expansion of a saturated vapor we obtain

$$\frac{\partial}{\partial g} \ln \frac{1}{Z} = \Delta\varphi_f = \frac{\bar{r}\Delta T}{RT_s^2}$$

when the supercooling is small and

$$\frac{\partial}{\partial g} \ln \frac{1}{Z} = \frac{\bar{r}}{R(T_s - \Delta T)} \ln \frac{T_s}{T_s - \Delta T}$$

when it is considerable.

Thus, in the case of adiabatic expansion from a state of saturation the relations between the two types of condensation centers are determined from the equation

$$\frac{I}{I'} = \frac{\rho\bar{r}}{2(2\pi)^{\frac{1}{2}} \frac{\sigma}{r} \left( \frac{T_s}{\Delta T} \right)^3 Ru \sqrt{RT} \frac{d\Delta T}{dl}} \quad (15)$$

when the supercooling is small, and

$$\frac{I}{I'} = \frac{\rho\bar{r} \left( \ln \frac{T_s}{T_s - \Delta T} \right)^3}{2(2\pi)^{\frac{1}{2}} \frac{\sigma}{r} Ru \sqrt{RT} \frac{d\Delta T}{dl}} \quad (16)$$

when the supercooling is arbitrarily large.

From these equations it is easy to see that  $I/I' > 1$  for ordinary values of the supercooling gradient ( $d\Delta T/dl$  usually fluctuates from  $1000^\circ \text{ K/m}$  to  $100^\circ \text{ K/m}$ ). This means that in the nozzles of steam turbines an important role is played by the condensation centers that appear as a result of the mobility of the boundary between stable and unstable droplets.

## NOTATION

$N(g)$  is the distribution characteristic of the equilibrium state of the vapor, i. e., the relation between the number of droplets and the number of molecules in a droplet in the equilibrium state of the vapor;  $f(g)$  is the distribution characteristic of the nonequilibrium state of the system, i. e., the relation between the number of droplets and the number of molecules in a droplet in the nonequilibrium state of the vapor;  $g$  is the number of molecules in the droplet;  $C$  is a constant approximately equal to the number of molecules in the system;  $\Delta\varphi = \varphi_B - \varphi_A$  is the difference of the chemical potentials of the liquid and vapor phases;  $b = \sigma(4\pi)^{1/3}(3v_B)^{2/3}$  is a coefficient reflecting the action of the surface tension forces;  $\sigma$  is the surface tension;  $k$  is Boltzmann's constant;  $v_A$  and  $v_B$  denote the specific volume per molecule in the vapor and liquid phases, respectively;  $m$  is the molecular mass;  $\mu$  is the molecular weight;  $\lambda$  is the latent heat of vaporization for a single molecule;  $\bar{r}$  is the latent heat of vaporization;  $T_s$  is the saturation temperature for the plane phase interface;  $T$  is the temperature;  $p$  is the pressure;  $\Delta T = (T_s - T)$  is the supercooling;  $\tau$  is the time;  $u$  is the flow velocity;  $\kappa$  is the adiabatic exponent;  $\rho$  is the density;  $s(g)$  is the surface of the drop;  $r$  is the radius of the drop.

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