THE SIZE OF CONDENSATION NUCLEI AND THE GROWTH OF DROPS IN A SUPERSATURATED VAPOR

A. G. Blokh, S. M. Bazarov,
and S. V. Varvarin

UDC 536.423.4

A derivation based on the condition of dynamic equilibrium between a molecular complex and molecules of a gas is given for equations which allow the determination of the size of condensation nuclei and their subsequent growth within free molecular motion.

1. Critical Size of Condensation Nuclei

The question of the critical size of drop formations can be approached not only from the phenomenological standpoint of thermodynamics [1] but also by examining the dynamics of interaction between clustered molecules and single gas molecules.

At any instant of time the change in the number of molecules g in a complex is determined by the number of molecules entering and leaving the complex. If n_+ molecules enter a complex during a time period $\tau_{g,n+}$ and n_- molecules leave it during a time period $\tau^*_{g,n-}$, then the change in the number of molecules in this complex can be expressed as

$$\frac{dg}{dt}=\frac{n_+}{\tau_{g,n_+}}-\frac{n_-}{\tau^*_{g,n_-}}. \tag{1}$$

We will consider the mechanism of successive collisions between the molecular complex and gas molecules. During the time τ_g one molecule enters the complex, while during the time τ^*_g one molecule leaves it. Therefore, (1) becomes

$$\frac{dg}{dt}=\frac{1}{\tau_g}-\frac{1}{\tau^*_g}. \tag{2}$$

When $\tau_g < \tau^*_g$, condensation occurs and the number of molecules in the complex increases ($dg/dt > 0$). When $\tau_g > \tau^*_g$, evaporation occurs and the number of molecules in the complex decreases ($dg/dt < 0$).

It is evident from Eq. (2) that the complex can exist in dynamic equilibrium only if the time of interaction of the molecules with the complex τ^*_g becomes equal to the time of free motion of the complex τ_g. Under these conditions $dg/dt = 0$, and the number of molecules in the complex remains constant.

Such a metastable complex will henceforth be called critical. The size of a critical complex r_{cr} is determined by the number of molecules it contains g_{cr} and the size of a molecule r_1:

$$r_{cr}=r_1\sqrt[3]{g_{cr}}. \tag{3}$$

The quantities $1/\tau g$ and $1/\tau^*_g$ characterize, respectively, the probability of survival or destruction of a stable complex.

Let us determine the time of interaction between a molecule and a complex containing (g + 1) molecules. According to the kinetic theory of fluids [1],

$$\tau^*_{g+1}=\tau_0\exp\left(\frac{U_0}{kT}\right), \tag{4}$$

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 19, No. 5, pp. 905-911, November, 1970. Original article submitted November 11, 1969.

where the period of natural vibrations

$$\tau_0 = \frac{\Delta}{\bar{c}_{1g}} .$$

Here T is the temperature, k is the Boltzmann constant, U_0 is the bond energy, and Δ is the width of the potential gap. The mean relative velocity is

$$\bar{c}_{1g} = \sqrt{\frac{8kT}{\pi m_1}\left(1 + \frac{1}{g}\right)},$$

where m_1 is the mass of one molecule. From this,

$$\frac{\tau_g^*}{\tau_2^*} = \sqrt{2\left(1 - \frac{1}{g}\right)}, \tag{4a}$$

where the lifetime of a complex containing two molecules (interaction time between two molecules during collision) is

$$\tau_2^* = \frac{\Delta}{4\sqrt{\frac{kT}{\pi m_1}}} \exp\left(\frac{U_0}{kT}\right). \tag{4b}$$

We then determine the free motion time for a complex containing g molecules. According to the kinetic theory of gases [2],

$$\tau_g = \frac{\lambda_g}{\bar{c}_{1g}} \text{ and } \tau_1 = \frac{\lambda_1}{\bar{c}_{11}} .$$

Here the mean free path length for a complex containing g molecules is

$$\lambda_g = \frac{1}{\pi (r_1 + r_g)^2} \cdot \frac{1}{n_1} = \frac{1}{\pi r_1 \left(1 + \sqrt[3]{g}\right)^2} \cdot \frac{1}{n_1} ,$$

and λ_1 is the free path length for a gas molecule; n_1 is the concentration of single gas molecules, r_g is the size of a complex containing g molecules.

We find that

$$\frac{\tau_g}{\tau_1} = \frac{4\sqrt{2}}{\left(1 + \sqrt[3]{g}\right)^2 \sqrt{1 + \frac{1}{g}}} , \tag{5}$$

where the free motion time for a molecule is

$$\tau_1 = \frac{\lambda_1}{4\sqrt{\frac{kT}{\pi m_1}}} . \tag{5a}$$

In Fig. 1 is shown the manner in which the absolute values of τ_g (curve 1) and of τ_g^* (curve 2) change as functions of the number of molecules in a complex. It can be seen here that, as g increases, the free motion time τ_g decreases asymptotically while the collision time τ_g^* reaches its highest level. When $g = g_{cr}$, then $\tau_g = \tau_g^*$ and the complex has reached its critical size.

As a result of random fluctuations, the number of molecules in a complex of critical size can vary. The addition of one molecule to a complex of critical size is accompanied by a decrease in τ_g relative to its critical value $\tau_{g_{cr}} = \tau_{g_{cr}}^*$. The quantity dg/dt then becomes positive and a spontaneous growth of the complex (condensation) has started. In this way, the threshold unstable complex during initial condensation is a complex containing (g_{cr} + 1) molecules. Such a complex will henceforth be called a condensation nucleus.

Conversely, the loss of one molecule makes a critical complex unstable, with τ_g becoming greater than τ_g^* and dg/dt < 0. The size of the complex now decreases spontaneously and evaporation takes place. In this way, the threshold unstable complex at the beginning of evaporation is one containing (g_{cr} − 1) molecules.

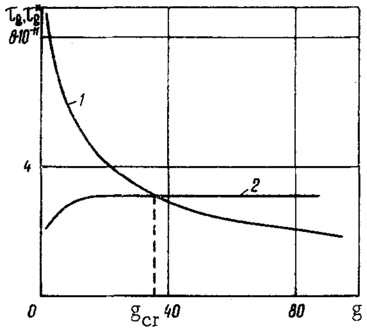

Fig. 1

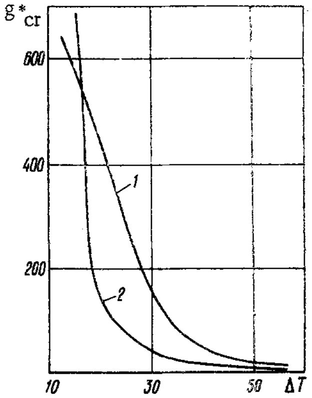

Fig. 2

Fig. 1. Change in the time (sec) of free motion τ_g and in the time (sec) of interaction between a molecule and a complex τ_g^*, as functions of the number of molecules in the complex g (pcs): 1) free motion time τ_g, 2) time of interaction between a molecule and the complex τ_g^*.

Fig. 2. Number of molecules in a condensation nucleus, as a function of the vapor subcooling temperature interval: 1) calculated by Eqs. (13) and (15); 2) according to Ya. I. Frenkel' [1].

Based on the foregoing discussion, we will determine the number of molecules contained in a complex of critical size.

Considering (4a) and (4b) as well as (5) and (5a), we write

$$\tau_g^* = \sqrt{2\left(1 - \frac{1}{g}\right)} \, \frac{\Delta}{4} \sqrt{\frac{\pi m_1}{kT}} \exp\left(\frac{U_0}{kT}\right), \tag{6}$$

and

$$\tau_g = \frac{\sqrt{2}}{\left(1 + \sqrt[3]{g}\right)^2} \cdot \frac{\lambda_1}{\sqrt{1 + \frac{1}{g}}} \sqrt{\frac{\pi m_1}{kT}}. \tag{7}$$

As was noted earlier, assuming $\tau_g^* = \tau_g$ and taking into account (6) and (7) will yield the equation:

$$\left(1 + \sqrt[3]{g_{cr}}\right)^2 \sqrt{1 - \frac{1}{g_{cr}^2}} = 4 \, \frac{\lambda_1}{\Delta} \exp\left(-\frac{U_0}{kT}\right), \tag{8}$$

which determines the number of molecules g_{cr} in a complex of critical size. When $g_{cr} \gg 1$, with the quantity $1/g_{cr}^2$ negligible compared to unity, we can write

$$\left(1 + \sqrt[3]{g_{cr}}\right)^2 = 4 \, \frac{\lambda_1}{\Delta} \exp\left(-\frac{U_0}{kT}\right) \tag{9}$$

or

$$g_{cr} = 8 \left[\sqrt{\frac{\lambda_1}{\Delta}} \exp\left(-\frac{U_0}{2kT}\right) - \frac{1}{2}\right]^3. \tag{10}$$

The radius of such a complex is

$$r_{cr} = 2 r_1 \left[\sqrt{\frac{\lambda_1}{\Delta}} \exp\left(-\frac{U_0}{2kT}\right) - \frac{1}{2}\right]. \tag{11}$$

Inserting the free path length of a molecule [2]

$$\lambda_1 = \frac{kT}{4\pi r_1^2 p}, \tag{12}$$

into (10) and (11), we arrive at

$$g_{\mathrm{cr}} = \left[\frac{1}{\sqrt{\pi\Delta}}\sqrt{\frac{kT}{p}}\exp\left(-\frac{U_0}{2kT}\right)-1\right]^3 \tag{13}$$

and

$$r_{\mathrm{cr}} = r_1\left[\frac{1}{\sqrt{\pi\Delta r_1}}\sqrt{\frac{kT}{p}}\exp\left(-\frac{U_0}{2kT}\right)-1\right], \tag{14}$$

which relate the magnitudes of g_{cr} and r_{cr} with the state properties of the gas: its pressure p and temperature T.

We now determine the radius of a condensation nucleus r^*_{cr} corresponding to the number of molecules in a complex

$$g^*_{\mathrm{cr}} = g_{\mathrm{cr}} + 1. \tag{15}$$

Using (3), we can write for these conditions:

$$r^*_{\mathrm{cr}} = r_1\sqrt[3]{g_{\mathrm{cr}} + 1.} \tag{16}$$

The formulas obtained here indicate that, knowing the saturation temperature T_∞ which corresponds to the vapor pressure p, one can, for every amount of vapor subcooling ΔT, determine without difficulty the size of a condensation nucleus r^*_{cr} and the number of molecules g_{cr} in a complex of critical size.

As an example, we determine the magnitudes of g^*_{cr} for water vapor at p = 0.5 bar.

The calculated values of g^*_{cr} are given in Fig. 2 as a function of the subcooling temperature interval ΔT. For comparison, the values of g_{cr} calculated by the known Ya. I. Frenkel' formula [1] are also shown here. It is evident that the number of molecules g^*_{cr} and thus the size of the condensation nucleus r^*_{cr}, as was to be expected, decreases considerably when the subcooling temperature interval ΔT increases. The widest discrepancy between values calculated by Eq. (1) and by the corresponding Ya. I. Frenkel' formula [1] is observed in the range of slight subcooling, when the condensation nuclei contain sufficiently larger numbers of molecules. As $\Delta T \to 0$, the size of a condensation nucleus according to Ya. I. Frenkel' becomes $r^*_{cr} \to \infty$, which corresponds to a flat separation surface. Under these conditions, calculations by the formulas derived here yield finite values for the radius of condensate drops. In the range of greater ΔT values, at the same time, the magnitude of g_{cr} calculated by Eq. (10) is several times greater than that of g_{cr} according to Ya. I. Frenkel' [1].

In our opinion, these discrepancies relate to the fact that the equations for g^*_{cr} and r^*_{cr} have been derived here from the concept of a dynamic equilibrium on a microscopic scale between molecular clusters and gas molecules, while the Ya. I. Frenkel' formula is based on the conditions of thermodynamic equilibrium in a macroscopic system.

2. Rate of Growth of Drops

When the free path length for a gas molecule λ_1 is much greater than the size of liquid drops r_g, then the steady-state heat and mass transfer between a drop containing g molecules and the vapor molecules is discrete in character and can be described by the equation:

$$qi_a = e_r T_g i_r - e_f T i_f \tag{17}$$

where q is the heat of condensation per molecule, i_f, i_a, and i_r are the quantities of molecules falling on a drop, absorbed, and reflected per unit time, and T_g, T are the drop and the gas temperature respectively.

The quantities of energy per one falling molecule (e_f) and per one reflected molecule (e_r) of gas in Eq. (17) can be expressed as [3]

$$e_f = \frac{1}{1-\gamma} kT \tag{18}$$

and

$$e_r = \frac{1}{1-\gamma} kT_g, \tag{19}$$

where γ is the adiabatic exponent.

Obviously,

$$i_{\mathrm{f}} = i_{\mathrm{a}} + i_{\mathrm{r}} . \tag{20}$$

Considering (18), (19), and (20), we can write (17) as follows:

$$\left(q + \frac{1}{\gamma - 1} kT_{\mathrm{g}}\right) i_{\mathrm{a}} = -\frac{1}{\gamma - 1} k\Delta T i_{\mathrm{f}} , \tag{21}$$

where

$$\Delta T = T_{\mathrm{g}} - T.$$

It follows from (21) that

$$qi_{\mathrm{a}} = \frac{1}{1 + \dfrac{kT_{\mathrm{g}}}{q(\gamma - 1)}} \cdot \frac{k\Delta T i_{\mathrm{f}}}{\gamma - 1} . \tag{22}$$

According to the kinetic theory of gases [2], the number of vapor molecules colliding every second with a drop of radius r_g is equal to

$$i_{\mathrm{f}} = \sqrt{2}\, \pi (r_1 + r_g)^2 \sqrt{\frac{8kT}{\pi m_1}} \left[1 + \left(\frac{r_1}{r_g}\right)^3\right]^{\frac{1}{2}} n_1. \tag{23}$$

when $r_1 \ll r_g$, this expression simplifies to

$$i_{\mathrm{f}} = \sqrt{2}\, \pi r_{\mathrm{g}}^2 \sqrt{\frac{8kT}{\pi m_1}}\, n_1. \tag{24}$$

Introducing here the heat-transfer coefficient

$$\alpha = \frac{\sqrt{2}}{4} \cdot \frac{k}{\gamma - 1} \sqrt{\frac{8kT}{\pi m_1}}\, n_1 \frac{1}{1 + \dfrac{kT_{\mathrm{g}}}{q(\gamma - 1)}} \tag{25}$$

and considering (24), we obtain from (22)

$$qi_{\mathrm{a}} = 4\alpha\pi r_{\mathrm{g}}^2 \Delta T. \tag{26}$$

Substituting

$$\beta = \frac{kT_{\mathrm{g}}}{q(\gamma - 1)} ,$$

and

$$\bar{c} = \sqrt{\frac{8kT}{\pi m_1}} ,$$

we have

$$\alpha = \frac{\sqrt{2}}{4} \cdot \frac{k}{\gamma - 1} n_1 \frac{\bar{c}}{1 + \beta} , \tag{27}$$

or, considering the equation of state for a gas,

$$\alpha = \frac{\sqrt{2}}{4(\gamma - 1)} R\rho \frac{\bar{c}}{1 + \beta} \tag{28}$$

where R is the gas constant and ρ is the gas density.

Using the results of [2], we write the kinematic viscosity of vapor as

$$\nu = \frac{1}{3} \lambda_1 \bar{c}. \tag{29}$$

Inserting the value of $\bar{c}$ from (29) into (28), we have

$$\alpha = \frac{3\sqrt{2}}{4(\gamma - 1)} \cdot \frac{\nu}{\lambda_1} R\rho \frac{1}{1 + \beta} . \tag{30}$$

Let us now determine α as a function of Knudsen and Prandtl numbers

$$\mathrm{Kn} = \frac{\lambda_1}{2r_g}; \quad \mathrm{Pr} = \frac{c_p \nu \rho}{\lambda_1}, \tag{31}$$

where c_p is the specific heat of a gas at constant pressure.

For this purpose, we transform (30) into

$$\frac{\alpha}{\alpha_0} = \frac{3\sqrt{2}}{4(\gamma-1)} \cdot \frac{\mathrm{Pr}}{\mathrm{Kn}} \cdot \frac{R}{c_p} \cdot \frac{1}{1+\beta}. \tag{32}$$

Here α_0 is the heat transfer coefficient for a sphere in a continuous stream.

Equation (32) represents the most general solution to this problem, in terms of the Pr and Kn numbers, the ratio R/c_p, the adiabatic exponent γ, and the parameter β accounting for the ratio of the energy per one molecule in a drop to the bond energy of this molecule.

According to Eq. (32), for given physical gas parameters (R, c_p, γ) the relative heat transfer coefficient is a function of two basic variables: the Kn number and β. When $\beta \approx 0$, Eq. (32) converts directly into the known G. Gyarmathy equation [4].

For the operating conditions of a stream turbine with water drops suspended in a water vapor atmosphere, we obtain from (32):

$$\frac{\alpha}{\alpha_0} \approx \frac{0.38}{1+\beta} \cdot \frac{1}{\mathrm{Kn}}. \tag{33}$$

Corresponding calculations by the G. Gyarmathy equation (for $\beta \approx 0$) [4] yield a numerical value of 0.32 for the coefficient in (32).

LITERATURE CITED

1. Ya. I. Frenkel', Kinetic Theory of Fluids [in Russian], Izd. AN SSSR, Moscow (1945).
2. D. Meier and M. Geppert-Maier, Statistical Mechanics [Russian translation], IL, Moscow (1952).
3. G. V. Lippman and A. Roshko, Elements of Gas Dynamics [Russian translation], IL, Moscow (1960).
4. G. Gyarmathy, Dissertation, Inst. fur Therm. Turbomasch., No. 6, (1962).