SIZE OF CONDENSATE NUCLEI IN A STREAM OF SUPERSATURATED VAPOR

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Analyzed is the effect of the relative vapor stream velocity on the size of condensate nuclei.

Many studies have been published so far [1-3 et al.] concerning the size of condensate nuclei in stationary supersaturated vapor. The results of these studies can be used for analyzing the process of initial phase transformation in a vapor stream, of course, but only under the condition that the relative velocity between the phases is zero.

In practice one usually encounters problemsof condensation in a vapor stream where droplets move relative to it. Quite understandably, the conditions of the vapor flow cannot but affect the kinetics of condensation. It has been shown in [4] that an important factor in the process of homogeneous condensation is the mean free-flow-time of a droplet. This mean free-flow-time will be defined as the mean time during which a droplet moves without colliding against vapor molecules, i.e., the time between two successive collisions of a droplet containing g molecules against single vapor molecules.

We will determine the mean free-flow-time τ_g of a droplet whose radius is r_g and which consists of g molecules, the radius of each molecule being r_1, when $g \gg 1$ and the relative velocity of the vapor stream is V_{1g}. For the purpose of analysis, we consider separately a fictitious spherical surface (Fig. 1) with the radius

$$r = r_g + r_1,$$

representing the effective collision surface between a droplet complex (radius r_g) and a vapor molecule (radius r_1), and we calculate the number of collisions between vapor molecules and this surface per unit time.

The surface of the hemisphere facing the vapor stream ($0 \leq \theta \leq \pi/2$) will be denoted by S_+, the back surface ($\pi/2 \leq \theta \leq \pi$) will be denoted by S_-. Elementary spherical zones on the front surface and on the back surface will be denoted by dS_+ and dS_-, respectively. The area of such an elementary zone on the given spherical surface is

$$dS = 2\pi r^2 \sin\theta d\theta. \tag{1}$$

Let us determine the number of molecules dn_+ colliding against an elementary surface element dS_+ per unit time. According to [5], we can write

$$dn_+ = n_1 \frac{V_m}{2\sqrt{\pi}} \{\exp(-\eta_n^2) + \sqrt{\pi}\,\eta_n [1 + \operatorname{erf}(\eta_n)]\} dS_+. \tag{2}$$

Analogously, the number of collisions dn_- against a surface element dS_- is

$$dn_- = n_1 \frac{V_m}{2\sqrt{\pi}} \{\exp(-\eta_n^2) - \sqrt{\pi}\,\eta_n [1 - \operatorname{erf}(\eta_n)]\} dS_-. \tag{3}$$

Here

$$V_m = \sqrt{\frac{2kT}{m_1}}$$

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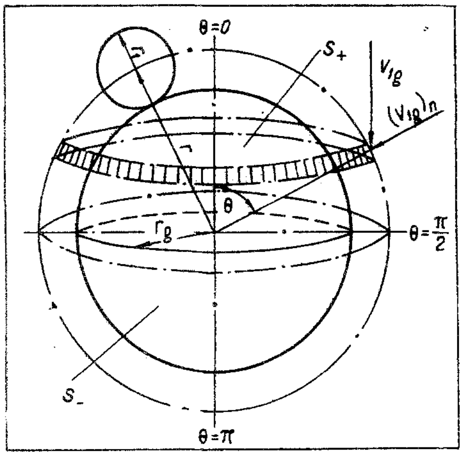

Fig. 1

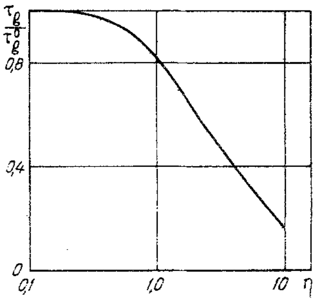

Fig. 2

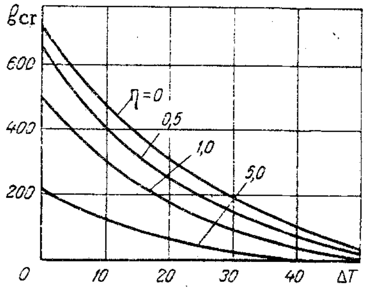

Fig. 3

Fig. 1. Diagram to show effective section through a colliding system (fictitious spherical surface).

Fig. 2. Variation in the relative mean free-flow-time of a droplet.

Fig. 3. Number of molecules in a condensate nucleus, as a function of the degrees subcool ΔT (°K) in water vapor.

is the most probable thermal velocity of vapor molecules. The quantity

$$\eta_n = \frac{(V_{1g})_n}{V_m}$$

characterizes the ratio of two velocities: the component of the relative vapor velocity $(V_{1g})_n$ normal to the surface element and the most probable thermal velocity of vapor molecules V_m.

The error function in (2) and (3) is

$$\operatorname{erf}(\eta_n) = \frac{2}{\sqrt{\pi}} \int_0^{\eta_n} \exp(-x^2)\, dx. \tag{4}$$

With the dimensionless relative vapor velocity

$$\eta = \frac{V_{1g}}{V_m} = \eta_n \frac{V_{1g}}{(V_{1g})_n},$$

we can write

$$\eta_n = \eta \cos\theta. \tag{5}$$

Having thus determined the number of collisions n_+ and n_- between vapor molecules and surfaces S_+, S_-, respectively, we find the total number of collisions

$$n = n_+ + n_-. \tag{6}$$

In order to determine n_+ and n_-, it is necessary to integrate expressions (2) and (3) with respect to S_+ and S_-, respectively. Taking into account (1) and (5), we obtain

$$n_+ = n_1 \sqrt{\frac{2kT}{\pi m_1}}\, \pi r^2 F_+(\eta), \tag{7}$$

$$n_- = n_1 \sqrt{\frac{2kT}{\pi m_1}}\, \pi r^2 F_-(\eta), \tag{8}$$

where

$$F_+(\eta) = \frac{\sqrt{\pi}}{2} \cdot \frac{\operatorname{erf}(\eta) + \eta^2 + 2\int_0^{\eta} x \operatorname{erf}(x)\, dx}{\eta}, \tag{9}$$

$$F_{-}(\eta)=\frac{\sqrt{\pi}}{2}\cdot\frac{\operatorname{erf}(\eta)-\eta^{2}+2\int\limits_{0}^{\eta}x\operatorname{erf}(x)\,dx}{\eta}. \tag{10}$$

With the aid of these relations, it is not difficult to determine the total number of molecules colliding against a droplet per unit time:

$$n=n_{1}\sqrt{\frac{8kT}{\pi m_{1}}}\,\pi r^{2}F(\eta), \tag{11}$$

where

$$F(\eta)=\frac{1}{2}\,[F_{+}(\eta)+F_{-}(\eta)]=\frac{\sqrt{\pi}}{2}\cdot\frac{\operatorname{erf}(\eta)+2\int\limits_{0}^{\eta}x\operatorname{erf}(x)\,dx}{\eta}. \tag{12}$$

When the relative vapor velocity $V_{1g}=0$, then $\eta=0$ and function $F(\eta)=1$. Under these conditions formula (11) becomes the well-known formula for the number of collisions between vapor molecules and a sphere of radius r_g in a stationary gaseous medium:

$$n_{0}=n_{1}\sqrt{\frac{8kT}{\pi m_{1}}}\,\pi r^{2}. \tag{13}$$

Knowing the number of collisions between a droplet and vapor molecules per unit time, we can easily determine the mean free-flow-time for a complex of g molecules:

$$\tau_{g}=\frac{1}{n}=\frac{1}{n_{1}\sqrt{\frac{8kT}{\pi m_{1}}}\,\pi r^{2}F(\eta)}. \tag{14}$$

When there is no relative motion, i.e., $\eta=0$, then formula (14) becomes the well-known formula for the mean free-flow-time of a droplet in stationary vapor:

$$\tau_{g}^{0}=\frac{1}{n_{1}\sqrt{\frac{8kT}{\pi m_{1}}}\,\pi r^{2}}. \tag{15}$$

With the aid of (14) and (15), we set up the ratios

$$\Phi(\eta)=\frac{\tau_{g}}{\tau_{g}^{0}}, \tag{16}$$

and

$$\Phi(\eta)=1/F(\eta). \tag{17}$$

The trend of τ_g/τ_g^0 as a function of η is well indicated by the curve in Fig. 2. As the dimensionless relative velocity of the vapor stream η increases, according to the graph, the quantity τ_g/τ_g^0 decreases. For low relative vapor velocities ($\eta \ll 1$) the first two terms in the Taylor series expansion of erf(x)

$$\operatorname{erf}(x)\approx\frac{2x}{\sqrt{\pi}}\left(1-\frac{x^{2}}{3}\right), \tag{18}$$

yield, after simple transformations,

$$\tau_{g}=\frac{\tau_{g}^{0}}{1+\frac{1}{3}\eta^{2}-\frac{2}{15}\eta^{4}}. \tag{19}$$

Formula (19) determines the mean free-flow-time of a droplet as a function of the relative vapor velocity at low values of η.

For high relative vapor velocities ($\eta \gg 1$) the first two terms in the asymptotic series expansion of erf(x)

$$\operatorname{erf}(x) \approx 1 - \frac{\exp(-x^2)}{x\sqrt{\pi}}, \tag{20}$$

yield a hyperbolic relation

$$\tau_g = \frac{2}{\sqrt{\pi}\,\eta}\,\tau_g^0. \tag{21}$$

Let us now determine the critical size of a condensate nucleus under the given conditions. For this it is necessary to establish what number of molecules in a droplet g_{cr} will produce a dynamic equilibrium between incoming and outgoing molecules.

As has been shown in [4], a droplet consisting of g_{cr} molecules may be in dynamic equilibrium with the vapor when the probability p_- of one droplet molecule evaporating is equal to the probability p_+ of one vapor molecule condensing. In accordance with the kinetic theory of liquids [1] and gases [5],

$$p_- \approx \frac{t}{\tau_g^*} \text{ and } p_+ \approx \frac{t}{\tau_g}. \tag{22}$$

Here

$$\tau_g^* = \frac{\Delta}{\sqrt{\frac{8kT}{\pi m_1}}} \exp\left(\frac{U_g}{kT}\right) \tag{23}$$

is the mean time of interaction between vapor molecules and a droplet. It follows from (22) that a complex of g_{cr} molecules may be in dynamic equilibrium with the ambient vapor when the mean time of their interaction τ_g^* becomes equal to the mean free-flow-time of the complex. The size of such a complex is determined by the number of molecules g_{cr} in it, namely

$$r_{cr} = 2r_1\left[\sqrt{\frac{1}{4\pi r_1^2 n_1}\cdot\frac{\Phi(\eta)}{\Delta}\exp\left(-\frac{V_g}{2kT}\right)} - \frac{1}{2}\right]. \tag{24}$$

Inserting into (24) the mean free-flow-path

$$\lambda_1 = \frac{1}{4\pi r_1^2 n_1}, \tag{25}$$

we obtain

$$r_{cr} = 2r_1\left[\sqrt{\frac{\lambda_1}{\Delta}\Phi(\eta)\exp\left(-\frac{V_g}{2kT}\right)} - \frac{1}{2}\right]. \tag{26}$$

The number of molecules in a droplet of critical size is then

$$g_{cr} = 8\left[\sqrt{\frac{\lambda_1}{\Delta}\Phi(\eta)\exp\left(-\frac{V_g}{2kT}\right)} - \frac{1}{2}\right]^3. \tag{27}$$

Unlike in [4], formulas (24) and (27) take into account the effect of the relative vapor velocity on r_{cr} and g_{cr}. For the condensation in a stationary medium ($V_{1g} = 0$ and $\eta = 0$) formulas (24) and (27) become directly the well-known formulas in [4].

The critical number of molecules g_{cr} as a function of degrees subcool ΔT is shown in Fig. 3 for water vapor under a pressure of 0.5 bar and at various values of η from 0 to 5. The graph indicates that at each value of η the number of molecules in a condensate nucleus decreases as the degrees subcool increase. As the dimensionless relative velocity η increases, the number of molecules in a critical-size droplet decreases continually. For low relative velocities ($\eta \ll 1$) Eqs. (12), (17), and (18) yield

$$r_{cr} = 2r_1\left[\sqrt{\frac{\lambda_1}{\Delta}\cdot\frac{1}{1+\frac{1}{3}\eta^2-\frac{2}{15}\eta^4}\exp\left(-\frac{V_g}{2kT}\right)} - \frac{1}{2}\right], \tag{28}$$

and

$$g_{cr} = 8\left[\sqrt{\frac{\lambda_1}{\Delta}\cdot\frac{1}{1+\frac{1}{3}\eta^2-\frac{2}{15}\eta^4}}\exp\left(-\frac{V_g}{2kT}\right)-\frac{1}{2}\right]^3 \tag{29}$$

For high relative velocities ($\eta \gg 1$) Eqs. (12), (17), and (26) yield

$$r_{cr} = 2r_1\left[\sqrt{\frac{\lambda_1}{\Delta}\cdot\frac{2}{\sqrt{\pi\eta}}}\exp\left(-\frac{V_g}{2kT}\right)-\frac{1}{2}\right] \tag{30}$$

and

$$g_{cr} = 8\left[\sqrt{\frac{\lambda_1}{\Delta}\cdot\frac{2}{\sqrt{\pi\eta}}}\exp\left(-\frac{V_g}{2kT}\right)-\frac{1}{2}\right]^3. \tag{31}$$

These formulas yield the values of r_{cr} and g_{cr} for two extreme cases of a two-phase flow: when the relative velocity between vapor and droplets is low and when the thermal velocity of vapor molecules is high.

NOTATION

Δ	is the width of potential gap;
k	is the Boltzmann constant;
m_1	is the mass of a molecule;
n_1	is the number of molecules per unit vapor volume;
T	is the absolute temperature of vapor;
V_g	is the energy of bond between a molecule and a complex;
t	is the time.

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