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FEATURES OF NUCLEATION KINETICS IN VAPOR-GAS MIXTURES AT INCREASED PRESSURES OF GAS

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The kinetics of nucleation in a vapor-gas mixture at increased pressures of the gas-ballast (at Knudsen numbers determined from the radius of a critical nucleus below unity) is theoretically investigated. Interpolation expressions for the nucleation rate at arbitrary Knudsen numbers are obtained.

Introduction. One of the basic assumptions of a classical nucleation theory in gases [1, 2] is the assumption that a metastable supersaturated vapor and a gas-ballast are spatially uniform. In this case the kinetics of nucleation can be described solely as a process of Brownian walk in the nucleus-size space [3].

From the viewpoint of the kinetic theory of gases [4] a vapor-gas system with a new phase nucleus may be considered locally spatially uniform in the case when the Knudsen number $Kn_0 = \lambda/R_0 >> 1$.

Since $R_0 \sim 10^{-9}$ m, the validity of the condition $Kn_0 >> 1$ is usually obeyed over a fairly wide range of pressures of the gas. However for a number of substances, mainly with a large molecular weight, the condition $Kn_0 >> 1$ is violated even at moderate pressures. So, for example, for dioctylphthalate the condition $Kn_0 \leq 1$ is attained at a pressure of the gas-ballast (helium) equal to $2 \cdot 10^6$ Pa [5]. Reaching the condition $Kn_0 < 1$ for other substances including water requires considerably higher pressures of the gas-ballast (usually helium) than has currently been attained on experimental stands for investigating the kinetics of nucleation [6].

At Knudsen numbers smaller than unity the local spatial uniformity in the vicinity of the new phase nucleus is violated and the necessity emerges to consistently describe the evolution of the function of distribution for the new phase nuclei f(g, t) in size g (number of molecules) and macroscopic vapor density n(x, t) close to the nucleus.

Mathematical Model of Nucleation Kinetics with $Kn_0 < 1$. The work [7] derives by the methods of nonequilibrium statistical thermodynamics [8] a system of equations describing the kinetics of nucleation with $Kn_0 < 1$. In Markov's approximation this system of equations has the form

$$\frac{\partial f(g, t)}{\partial t} = \frac{\partial}{\partial g}\left[f\left(L_{11}\frac{\partial}{\partial g}(\ln f + \Delta\Phi(g)\beta) + \int \frac{\nabla n}{n} J_{11}(x)\, d^3x\right)\right] = -\frac{\partial}{\partial g} I, \tag{1}$$

$$\frac{\partial n(x, t)}{\partial t} = \operatorname{div}\left[D\nabla n + \mathbf{J}_{11}(x)\int f(g, t)\frac{\partial \Delta\Phi}{\partial g}\beta dg\right]. \tag{2}$$

In the kinetic equation (1), $\Delta\Phi(g)$ is the free energy of formation of the new phase nucleus consisting of g molecules [1, 2], I is the nucleation rate; $\beta = 1/kT$, where k is the Boltzmann constant, T is the temperature. In [7] a representation in the Green-Kubo form is obtained for all kinetic coefficients [8, 9], which has enabled us to find an exact relation between the kinetic coefficients from (1)

$$L_{11} = \int d^3x \operatorname{div} \mathbf{J}_{11}(x), \tag{3}$$

where $\int d^3x$ is integration over the spatial variables outside the nucleus. In its turn the kinetic coefficient L_{11} with $Kn_0 << 1$ is expressed using the diffusion factor D of the vapor in the mixture as [7]

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$$L_{11} = 4\pi R_0 D n_0, \tag{4}$$

where n_0 is the equilibrium vapor density in the system. The vector $\mathbf{J}_{11}$ is equal up to a constant to the integral with respect to time of the correlation function between the flows of vapor molecules through the nucleus surface and in the vicinity of the point with the coordinate x.

In the approximation of spherical symmetry of the vapor state close to the nucleus, assuming that the origin of coordinates coincides with the nucleus center, $\mathbf{J}_{11}$ is to depend only on the distance **r**. Then by using the method proposed in [9] we can obtain an approximate solution for $\mathbf{J}_{11}$, nevertheless satisfying the relation (3), which plays the role of the law of sums [8]. As is shown in [7], in view of (4) it has the form

$$\mathbf{J}_{11}(\mathbf{r}) = \frac{Dn_0}{3R_0} \exp\left(-\frac{(r - R_0)}{\lambda}\right) \frac{\mathbf{r}}{|\mathbf{r}|}. \tag{5}$$

From (5) it follows that at distances of the order λ the correlation function tends to zero in accordance with the usual physical notions of the kinetic theory of gases. Thus, in Eqs. (1) and (2) the terms in which $\mathbf{J}_{11}$ enters take account of the contribution of the Knudsen layer close to the nucleus. It is pertinent to note that an accurate calculation of $\mathbf{J}_{11}$ is currently an unsolved problem of statistical physics.

A complete mathematical investigation of the nonlinear system of Eqs. (1) and (2) seems a considerable challenge. Since we are interested in the influence of Knudsen layers on the stationary kinetics of nucleation we will further restrict ourselves only to stationary solutions of this system of equations.

We will point out that with $\mathrm{Kn}_0 \ll 1$ we may disregard the terms containing $\mathbf{J}_{11}$ in Eqs. (1) and (2). In this case, as follows from (1), the kinetics of nucleation can again be described solely as a process of Brownian walk in the nucleus-size space. Only the value of the diffusion factor in the nucleus-size space varies in comparison with a free molecular regime. With $\mathrm{Kn}_0 \ll 1$ it, as has already been mentioned, is determined by formula (4). The solution (1) with $\mathrm{Kn}_0 \ll 1$ reduces just to varying the diffusion factor in the known Zeldovich solution [2].

Abandoning the condition $\mathrm{Kn}_0 \ll 1$, as follows from (1), requires taking account of the influence of Knudsen layers. For this we will find an approximate analytical solution of Eqs. (1) and (2). In doing so the vapor density field n(r) can be found from (2) without regard for the Knudsen layer, i.e., assuming in (2) $\mathbf{J}_{11} = 0$. When solving the kinetic equation we will take account of corrections to the diffusion approximation in a first approximation with respect to the Knudsen number by using the density field n(r) found earlier.

The spherically symmetric stationary solution (2), satisfying the boundary conditions

$$n(r)|_{r=R} = n_1, \tag{6}$$

$$n(r)|_{r=\infty} = n_0, \tag{7}$$

where n_1 is the density of the saturated vapor above the nucleus of radius R, has the form

$$n(r) = \frac{(n_1 - n_0) R}{r} + n_0. \tag{8}$$

Using (5) and (8) we may calculate the integral $\int \nabla n \mathbf{J}_{11}/n dx$ enteging in (1). In view of the dependence of $\mathbf{J}_{11}$ on r it is equal to

$$\int \frac{\nabla n}{n} \mathbf{J}_{11}(r)\, d^3x = -\frac{4\pi D n_0 \lambda}{3} \frac{(n_1 - n_0)}{n_1} + O(\mathrm{Kn}_0). \tag{9}$$

It is common knowledge that the chemical potential of vapor μ accurate to an addition, insignificant for our purposes, is equal to [10]:

$$\mu = \beta^{-1} \ln n(r). \tag{10}$$

Now by using (10) the quantity $(n_1 - n_0)/n_1$ can be represented as $(n_1 - n_0)/n_1 \approx \beta(\mu_1 - \mu_0) = \beta(\partial\Delta\Phi/\partial g)$, where μ_1 and μ_0 are the chemical potentials on a per-molecule basis in the nucleus and in the uniform vapor. As a result we have

$$\int \frac{\nabla n}{n} \mathrm{J}_{11} d^3x = -\frac{L_{11}\,\mathrm{Kn}}{3} \frac{\partial \Delta\Phi}{\partial g} \beta + O(\mathrm{Kn}_0). \tag{11}$$

We call attention to the fact that the integral (11) changes sign depending on the nucleus size (number of molecules) in comparison with critical, for which it becomes zero. The contribution of the Knudsen layer, as it follows from (11) and (1), reduces to varying the height of the thermodynamic barrier, above which Brownian diffusion proceeds in the nucleus-size space. The geometric sizes of the new phase clusters, substantial for the kinetics of nucleation, as can easily be shown, coincide to a very high accuracy with the geometric size of the critical nucleus. This circumstance is also used in calculating the integral in (9).

The kinetic equation (1) in view of (11) can be written now as

$$\begin{aligned} &\frac{\partial}{\partial g}\left[fL_{11}\frac{\partial}{\partial g}(\ln f + \beta\Delta\Phi(g)(1 - \mathrm{Kn}_0/3))\right] = \\ &= \frac{\partial}{\partial g}\left[fL_{11}\frac{\partial}{\partial g}(\ln f + V)\right] = 0. \end{aligned} \tag{12}$$

The boundary condition to the kinetic equation (12) at small g is chosen from the condition that the flow in the nucleus-size space I is equal to zero, i.e.,

$$f(g)|_{g\to 0} = C\exp(-V), \tag{13}$$

where C is the normalizing constant to the distribution function. At large g we have the condition, common in nucleation theory,

$$f(g)|_{g\to\infty} = 0. \tag{14}$$

It should be pointed out that the boundary condition (13) is a natural generalization of the boundary condition taken in classical nucleation theory [1, 2, 11].

By substituting the variable $f(g) = C\exp(-V)y$ Eq. (12) with the boundary conditions (13) and (14) can be integrated.

The variable y first, introduced in [2], is a "slow" variable in nucleation theory. Its typical plot is given in Fig. 1. The expression for the nucleation rate has the form

$$I = CL_{11}\exp\left(-\beta\Delta\Phi(g^*)\left(1 - \frac{\mathrm{Kn}_0}{3}\right)\right)\sqrt{\frac{\beta(\mu_0 - \mu_1)}{6\pi g^*(1 - \mathrm{Kn}_0/3)}},$$

or in the approximation, linear with respect to Kn, to the nucleation rate in a purely diffusion regime I_D

$$I = I_D\left(1 + \frac{\Delta\Phi(g^*)\,\mathrm{Kn}_0\,\beta}{3}\right), \tag{15}$$

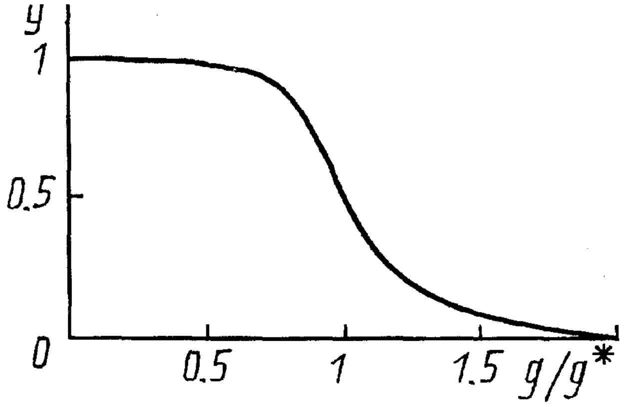
where

$$I_D = CL_{11}\exp(-\Delta\Phi(g^*)\beta)\sqrt{\frac{\beta(\mu_0 - \mu_1)}{6\pi g^*}}. \tag{16}$$

When deriving (15) it was expected that the normalizing constant C from (13) practically coincides with the normalizing constant for the distribution function from (16).

As follows from (15), taking account of the Knudsen layer close to the new phase nuclei increases the nucleation rate I, the value of I being substantially affected by the variation in the height of the effective thermodynamic barrier in Eq. (12).

Nucleation Rate at Arbitrary Knudsen Numbers. It is well known that with Knudsen numbers $\mathrm{Kn}_0 \gg 1$ the rate of isothermal nucleation I_f is prescribed by the expression [1, 2]



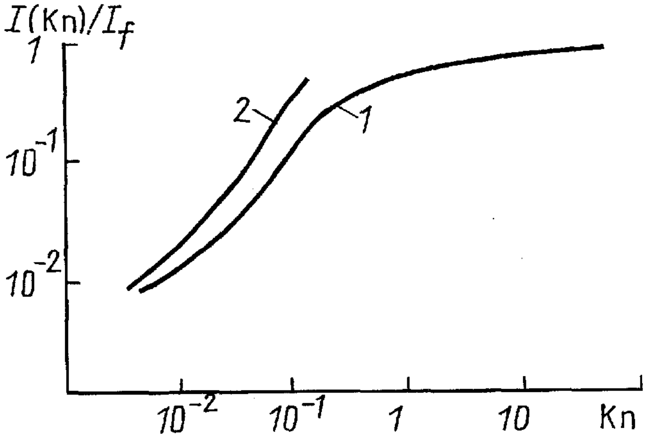


Fig. 1. Typical dependence of the "slow" variable y = f(g)/C exp(-V) on the number of molecules g in the new phase nuclei in the case of stationary kinetics of nucleation.

Fig. 2. Results of calculating the ratio of the nucleation rate I(Kn) to the nucleation rate in the free molecular regime I_f depending on the Knudsen number: 1) calculation with (22), $\gamma = 1.5$; 2) calculation with (15), $,\Delta\Phi(g^*)\beta = 50, \gamma = 1.5$.

$$I_f = 4\pi R_0^2 n_0 \sqrt{\frac{kT}{2\pi m}} \exp\left(-\Delta\Phi(g^*)\beta\right) \sqrt{\frac{\beta(\mu_0 - \mu_1)}{6\pi g^*}}. \tag{17}$$

We point out that I_f does not depend on the pressure of the gas-ballast. For intermediate numbers $Kn_0 \sim 1$ the structure of the kinetic equation for the distribution function of the new phase nuclei and an explicit form of the kinetic coefficients are currently unknown [12]; because of this, making use of expressions (15) and (17), we will find an interpolation expression for the nucleation rate I(Kn) with fixed supersaturation. For this we will apply Pade's approximant method [13]. We previously took into account that the diffusion factor D can be represented as [4]

$$D = \frac{\lambda}{4} \sqrt{\frac{8kT}{\pi m}} \gamma,$$

where γ is an adjusting coefficient of the order of unity. Then, comparing (17) and (16), we have

$$I_D = I_f \, \mathrm{Kn} \, \gamma. \tag{18}$$

We will represent the interpolation dependence of the nucleation rate I(Kn) on the Knudsen number in the form [I/I] of Pade's approximant:

$$I(\mathrm{Kn}) = \frac{a_0 + a_1 \mathrm{Kn}}{1 + b_1 \mathrm{Kn}}. \tag{19}$$

For determining the three unknown coefficients we will impose natural conditions, which make it possible to determine them:

$$I(\mathrm{Kn}) = I_f; \quad \mathrm{Kn} \to \infty, \tag{20}$$

and using (18) we obtain with Kn→ 0

$$I(\mathrm{Kn}) = I_f \gamma \, \mathrm{Kn}. \tag{21}$$

From (20) we obtain $a_1/b_1 = I_f$, and from (21) accurate to the first-order terms with respect to Kn, $a_0 = 0$, $a_1 = I_f\gamma$.

Now the interpolation formula (19) can be written as

$$\frac{I(\mathrm{Kn})}{I_f} = \frac{\gamma\,\mathrm{Kn}}{1 + \gamma\,\mathrm{Kn}}. \quad (22)$$

Figure 2 gives the dependence of $I(\mathrm{Kn})/I_f$ on the Knudsen number with $\gamma = 1.5$, calculated using (22) [5]. Curve 2 is obtained with $\Delta\Phi(g^*)\beta = 50$ [5]. Expression (22), unlike (15), does not depend on the value of $\Delta\Phi(g^*)\beta$. The proximity of curves 1 and 2 at small g indicates sufficiently high reliability of expression (22). We note that Pade's approximant method enables us to obtain other interpolation expressions for the nucleation rate, including those which take account of the derived relation (15).

CONCLUSIONS

1. Within the framework of a mathematical model of nucleation kinetics, taking account of a local spatially nonuniform state of a vapor-gas mixture close to the new phase nucleus the influence of Knudsen layers is investigated at increased pressures of the gas. Within the framework of perturbation theory first-order corrections with respect to the Knudsen number are found to the expression for the stationary nucleation rate (15).

2. The interpolation formula for the nucleation rate at arbitrary Knudsen numbers is obtained by Pade's approximant method (22). It is shown that the nucleation rate depends on the gas pressure if $\mathrm{Kn} \leq 10$ ($\mathrm{Kn} \sim P^{-1}$) and decreases as the pressure of the gas-ballast increases.

NOTATION

λ, mean free path of vapor molecules; R_0, critical nucleus radius; $f(g, t)$, function of distribution of new phase nuclei in size (number of molecules); $n(x, t)$, vapor density; I_f, nucleation rate in a free molecular regime; g^*, number of molecules in the critical nucleus; $I(\mathrm{Kn})$, nucleation rate with an arbitrary Knudsen number.

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