

The homogeneous nucleation in an optical radiation field

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The physical and mathematical model of homogeneous nucleation kinetics in a supersaturated vapor in an optical radiation field has been developed. It is of interest for the modern atmosphere research techniques and also from the standpoint of partial control of the nucleation process. A peculiarity of this problem lies in the fact that the temperature of nucleus differs from the equilibrium temperature of a vapor, a fact that can be explained either by the absorption of the light by the particle or by removal of the latent heat of phase transition.

1. Statement of the problem

Let us consider the supersaturated vapor at pressure p_v and temperature T_0 , in which monochromatic electromagnetic radiation with a wave length λ_0 is propagated. Let p_0 be the pressure of saturated vapor at the equilibrium temperature T_0 . The dimensionless parameter $s = p_v / p_0$ is relative supersaturation of the vapor.

We consider the spontaneous nucleation. Let the cluster of radius r , containing g molecules, was formed. Then the expression for nonisothermal work of nucleation has the form (Bashkirov and Fisenko, 1981)

$$\Delta\hat{O}(r, T_p) = (\mu_p - \mu_v)g + 4\pi\sigma r^2 + cg(\langle T_S \rangle - T_0) \left(\frac{L}{cT_0} - 1 \right), \quad (1)$$

where μ_p and μ_v are the chemical potentials per molecule of cluster and vapor respectively, σ is the surface tension, c is the heat capacity per condensed phase molecule, $\langle T_S \rangle$ is the particle temperature averaged over surface of the particle and L is the latent heat of phase transition per condensed phase molecule. Two first terms characterize the work of nucleation in isothermal system (Lifshitz and Pitaevskii, 1981, Piskunov, 2000) and the third term takes into account change of the particle temperature due to absorption of optical radiation and latent heat of phase transition. Note that the unknown temperature of the nucleus generally depends on thermophysical, optical and kinetic properties and on radiation characteristics.

The statistically equilibrium distribution n_g of particles over the sizes is defined by the formula

$$n_g = N_0(g) \exp \left[- \frac{\Delta\hat{O}(g, \langle T_p \rangle)}{kT_0} \right], \quad (2)$$

where $N_0(g)$ is the normalization factor proportional to numerical density of vapor's molecules n_v . The nonequilibrium size distribution of the particles f_g is described by the Fokker-Plank kinetic equation. The steady-state solution of this equation with boundary conditions $f_g/n_g \rightarrow 1$ at $r \rightarrow 0$ and $f_g/n_g \rightarrow 0$ at $r \rightarrow \infty$ has the form (Lifshitz and Pitaevskii, 1981, Piskunov, 2000):

$$\frac{f_g}{n_g} = J \int_g^{\infty} \frac{dg}{\beta_g n_g}. \quad (3)$$

Here J is the nucleation rate, β_g is the number of vapor molecules absorbed per unit time by particles consisting of g molecules. In the free-molecule regime, in which the mean free path of vapor molecules is much greater than the radius of nucleus, the value of β_g is calculated using the Maxwell velocity distribution function of vapor molecules

$$\beta_g = \alpha \pi r^2 n_v v_t, \quad v_t = \left(\frac{8kT_0}{\pi m_v} \right)^{1/2}, \quad (4)$$

where α is the evaporation – condensation coefficient, k is the Boltzmann constant and m_v is the mass of vapor molecule.

The nucleation rate is defined from expression (3). In case of $r \rightarrow 0$ we have

$$J = \left(\int_0^{\infty} \frac{dg}{\beta_g n_g} \right)^{-1}. \quad (5)$$

Thus, the critical radius $r_{\bar{n}}$ of the nucleus and nucleation rate J can be calculated if the particle temperature T_p is known.

2. Temperature of the nucleus

The temperature inside the particle and on its surface is described by a heat-conductivity equation (Chernyak, 1995)

$$-\lambda_p \Delta T_p = Q, \quad (6)$$

where λ_p is the particle heat-conductivity coefficient. The volumetric energy generation rate in the case of the plane monochromatic wave of λ_0 length has the form (Chernyak, 1995)

$$Q = \frac{4\pi}{\lambda_0} n \chi I B(\rho, \theta), \quad B(\rho, \theta) = \frac{|\mathbf{E}(\rho, \theta)|^2}{E_0^2}. \quad (7)$$

Here n and χ are, respectively, the refractive and absorptive indexes ($m = n + i\chi$ is the complex refraction index), ρ is the radial coordinate from the particle centre, θ is the

polar angle, $\mathbf{E}(\rho, \theta)$ is the local electric field strength inside the particle, \mathbf{E}_0 is the incident electric field strength and I is the intensity of radiation; $B(\rho, \theta)$ has been averaged over the azimuthal angle φ .

The boundary conditions to the equation (6) require the temperature limit at the particle centre and continuity of radial heat flux at its surface:

$$\left[q_0 + Lj_0 + \varepsilon\sigma_S(T_s^4 - T_0^4) + \lambda_p \frac{\partial T_p}{\partial \rho} \right]_{\rho=r} = 0, \quad (8)$$

where j_0 and q_0 are, respectively, the radial vapour molecular flow and heat flux on the surface of the particle, ε is the emissivity and σ_S is the Stefan-Boltzmann constant.

If f is the velocity distribution function of the vapour molecules, then at $\rho = r$ we have

$$j_0 = \int v_\rho f \, d\mathbf{v}, \quad q_0 = \frac{m_v}{2} \int (v_\rho - u_\rho)(\mathbf{v} - \mathbf{u})^2 f \, d\mathbf{v}, \quad (9)$$

where \mathbf{u} is the macroscopic velocity of vapour molecules and \mathbf{v} is the velocity of vapour molecule.

Let us assume that the part α of the vapor molecules is evaporated in an equilibrium manner according to the Maxwell distribution function f_S with the surface temperature T_S and with the corresponding number density n_s of saturated vapor, and the part $(1 - \alpha)$ is reflected without having been condensed on collision with the particle. The velocities of the reflected vapor molecules are distributed according to Maxwell's law f_r . Then the boundary condition for the distribution function has the form

$$f^+ = \alpha f_S + (1 - \alpha) f_r, \quad \rho = r, \quad v_\rho > 0, \\ f_{S,r} = n_{S,r} \left(\frac{m_v}{2\pi k T_S} \right)^{3/2} \exp\left(-\frac{m_v v^2}{2k T_S} \right), \quad (10)$$

where the unknown number density n_r of vapor molecules reflected from the surface of the particle can be found from the balance relation for the mass vapor fluxes at the surface (Chernyak, 1995).

Let us assume that the particle surface temperature T_S is slightly different from that for the vapor equilibrium temperature T_0 , i.e. $\tau_S = (T_S - T_0)/T_0 \ll 1$. In this case the temperatures T_S, T_0 and corresponding equilibrium number densities n_S, n_0 satisfy the linearized Clapeyron-Clausius equation

$$\frac{n_S}{n_0} = \exp(\delta \langle \tau_S \rangle), \quad \delta = \frac{L}{k T_0}, \quad (11)$$

The velocity distribution function f_0 of the vapor molecules at a great distance from the particle has the form

$$f_0 = sn_0 \left(\frac{m_v}{2\pi k T_0} \right)^{3/2} \exp \left(- \frac{m_v v^2}{2k T_0} \right). \quad (12)$$

Generally, the velocity distribution function at any point can be found from the solution of the Boltzmann equation. But we consider the free-molecule regime, in which the mean free path of molecules is much greater than the radius of nucleus. In this case we can ignore the perturbation of the distribution function for the molecules incident upon a particle due to collisions with emitted molecules. Therefore, the distribution function of incident molecules is the same as the distribution function at a great distance from the particle (12).

Analytical solution of the equations (6)–(12) is possible only under condition that $\delta \langle \tau_S \rangle \ll 1$. In this approximation we obtain

$$\begin{aligned} \langle \tau_S \rangle &= \frac{1}{A} \left[\alpha \left(1 + \frac{1}{2} \delta - \frac{5}{4} s + \frac{5}{8} \alpha (s-1) \right) (s-1) + \frac{K_a I}{2 p_0 v_t} \right], \\ A &= \frac{1}{2} \alpha \left(\delta^2 - \frac{5}{4} \delta + 3 - \frac{5}{8} \alpha s \right) - (1-\alpha) \left[s \left(\frac{5}{8} \alpha + \frac{5}{4} \alpha \delta - 1 \right) - \frac{15}{8} \alpha \delta \right] + \frac{8 \varepsilon \sigma_S T_0^4}{p_0 v_t}. \end{aligned} \quad (13)$$

Here K_a is the efficiency factor of the radiation absorption, I is the intensity of radiation. We can see that the temperature of the particle differs from the equilibrium temperature of a vapor, the fact that can be explained either by the absorption of the latent heat of phase transition by the particle (first term) or by the absorption of the radiation by the particle (second term).

3. Critical nucleation center and nucleation rate

Let v_m be average volume per condensed phase molecule. Then the number of molecules in the particle is $g = 4\pi r^3 / (3v_m)$. Taking into account (13), the expression (1) for the work of nucleation can be written in the following form

$$\Delta \hat{O}(r, T_p) = \left[\mu_p - \mu_v + T_0 (\delta k - c) \langle \tau_S \rangle \right] \frac{4\pi}{3v_m} r^3 + 4\pi \sigma r^2. \quad (14)$$

The radius r_c of critical nucleus center is defined from the condition of maximum of $\Delta \Phi$ at $r = r_c$. Equating to zero the derivative of the $\Delta \Phi$ with respect to r , we find

$$r_c = \frac{2\sigma v_m}{\mu_v - \mu_p - T_0 (\delta k - c) \langle \tau_S \rangle}. \quad (15)$$

The Frenkel - Zeldovich's classical formula for isothermal system (Lifshitz and Pitaevskii, 1981, Piskunov, 2000) is evident from Eq. (15) at by assuming that $\langle \tau_S \rangle = 0$.

Maximum value of the $\Delta \Phi$ function is the following

$$\Delta\Phi_m \equiv \Delta\Phi(r=r_c) = \frac{4}{3}\pi r_c^2 \sigma. \quad (16)$$

For calculation of nucleation rate J we shall take into account that integrand in (5) has a sharp peak in neighborhood of $g = g_c$ (g_c is the number of molecules consisting in the critical nucleus center). Using the saddle-point method, we obtain

$$J = \frac{\alpha}{2} n_v v_m v_t n(g_c) \sqrt{\frac{\sigma}{kT_0}}, \quad n(g_c) = N_0(g_c) \exp\left(-\frac{\Delta\hat{O}_m}{kT_0}\right). \quad (17)$$

The Frenkel - Zeldovich's classical formula for isothermal system is evident from Eqs. (16) and (17) again at by assuming that $\langle\tau_s\rangle = 0$.

4. Discussion

It follows from Eq. (15) that absorption of radiation by the formed nucleus stimulates its evaporation and hence leads to increase in the minimal size at which this nucleus appears viable and continues to grow. At particular value of radiation intensity $I = I_m$ the radius of critical nucleus should be the infinite. Physically it means that occurrence of viable nucleation centers in supersaturated vapor at $I \geq I_m$ is impossible. From Eqs. (13) and (15) we can see that

$$I_m K_a = 2p_0 v_t \left[\frac{Ak \ln s}{\delta k - c} - \alpha \left(1 + \frac{1}{2}\delta - \frac{5}{4}s + \frac{5}{8}\alpha(s-1) \right) (s-1) \right]. \quad (18)$$

Here we have taken into account that $\mu_v - \mu_p = kT_0 \ln s$.

It follows from expressions (16) and (17) that in the field of optical radiation the nucleation rate decreases. Quantitative estimations can be made for specific system at preset values of determining parameters.

We now make some numerical estimates for a specific system under typical conditions. Let us consider supersaturated water vapor. The values of determining parameters are

$$T_0 = 296K, \quad p_0 = 2,81 \cdot 10^3 Pa, \quad L = 7,31 \cdot 10^{-20} J, \quad s = 3, \\ c = 12,6 \cdot 10^{-23} J/K, \quad \alpha = 1, \quad \sigma = 0,0723 N/m.$$

The calculation with the formula (18) gives that the maximum of radiation intensity is $I_m K_a = 1.36 \times 10^7 W/m^2$.

The results of calculations for the radius r_c are presented in Table 1.

Table 1. The radius of critical nucleus as a function of radiation intensity.

$IK_a \times 10^{-4} W/m^2$	0	1	10	50	10^2	$5 \cdot 10^2$	10^3
$r_c \times 10^9, m$	4.48	4.49	4.52	4.64	4.84	7.09	17.0

It is seen that the dependence of the critical radius on the radiation intensity becomes appreciable only at $IK_a \geq 10^5 \text{ W/m}^2$.

Let J_0 be the nucleation rate at $I = 0$. The dependence of the quantity J/J_0 on the radiation intensity is presented in figure below.

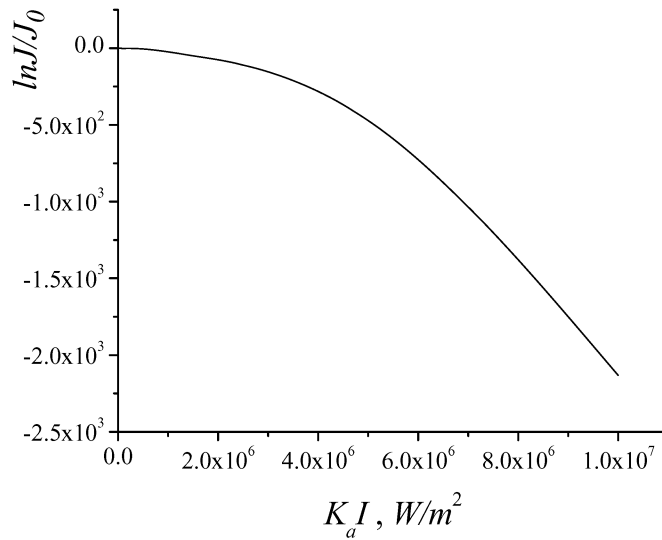


Fig.1. The nucleation rate as a function of radiation intensity.

As one would expect, the nucleation rate decreases as the radiation intensity increases. The calculation shows that severe decrease of the nucleation rate occurs at $IK_a \geq 1 \times 10^4 \text{ W/m}^2$.

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