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Light-induced evaporation and condensation growth of aerosol particles

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The nonisothermal evaporation and condensation of a particle suspended in a vapor-gas mixture under the effect of resonant optical radiation is studied. A traveling light wave is absorbed by the aerosol particle and velocity selectively by vapor molecules. The dependence of the evaporation or condensation rate on optical and thermophysical properties of the particle and gaseous molecules is studied. The free-molecule regime is examined.

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I. INTRODUCTION

The study of phenomena related to the effect of optical radiation on submicrometer particles is of fundamental importance in astrophysics and are of interest in connection with laser monitoring of the atmosphere. In particular, the evaporation of aerosols in the field of optical radiation is one of the main processes determining the time it takes for an aerodispersion system to clear up.

A fine macroscopic particle suspended in a mixture consisting of its own vapor and a noncondensing gas is considered. When the particle is irradiated by optical radiation, it heats up, thus destroying the phase equilibrium, and begins to evaporate. The kinetic theory of radiative evaporation of an aerosol particle absorbing radiation has been presented, in particular, in Ref. [1].

Velocity-selective excitation of vapor molecules can be one more cause of the evaporation or condensation growth of aerosol particles. Let the radiation be a traveling light wave whose frequency is close to that of an electronic or vibrational-rotational transition of a vapor molecule. Due to the Doppler effect, velocity-selective absorption of radiation takes place. The effective resonant velocity interval $\Delta\mathbf{v}$ is determined by the condition that $\mathbf{k}\cdot\Delta\mathbf{v}\sim\Gamma$, where $\mathbf{k}$ is the wave vector, and Γ is the homogeneous linewidth of the transition. The molecules that absorb radiation become excited and change their transport properties, in particular, the kinetic cross sections. If excited and unexcited vapor molecules interact differently with the molecules of the buffer (nonabsorbing and noncondensing) gas, the Maxwell velocity distribution of the vapor molecules is distorted [2]. As a result, the temperature of the vapor can be higher or lower than the equilibrium temperature of the system [3,4]. In the first case the aerosol particle evaporates, and in the second it grows due to the condensation of the vapor.

Another possible reason for the breakdown of the phase equilibrium is the dependence of the collision rate on the quantum state of the molecules. The change of the kinetic cross sections (or the mean free path) of the molecules that absorb radiation leads to modification of the Knudsen layer structure. The effective thickness of the Knudsen layer for the exited and unexcited molecules is different. As a result, the dynamic equilibrium between evaporation and condensation will be broken. The aerosol particle will be evaporating or growing depending on specific conditions.

The dependence of the probability of condensation at collisions of molecules with the particle surface on their quantum state is another reason of violation of phase equilibrium. If the condensation coefficient of the molecules that have absorbed radiation is increased, condensation processes are dominant and the particle grows. In the opposite case, in which the probability of condensation of the excited molecules is lower than that of the unexcited molecules, the particle evaporates.

The kinetic theory of isothermal evaporation and condensation growth of an aerosol nonabsorbing particle in a field of resonant optical radiation has been presented in Ref. [5]. The model ignored a change of the particle temperature. But generally, the temperature of the particle differs from the equilibrium temperature of a gas, a fact that can be explained either by the absorption of the light by the particle or by removal of the latent heat of evaporation.

In this paper the nonisothermal evaporation and condensation growth of an absorbing particle suspended in a vapor-gas mixture, in which the vapor molecules are velocity selectively excited by resonant optical radiation, is studied.

II. STATEMENT OF THE PROBLEM

Let us consider a spherical particle suspended in a mixture consisting of the vapor of this particle and a noncondensing gas. The radius r_0 of the particle is much greater than the radius of a critical nucleation center. The system is in thermodynamic equilibrium at temperature T_0.

We irradiate the system with monochromatic light. A traveling light wave is propagating along the axis z (Fig. 1). Let the radiation be absorbed by the vapor molecules in an electronic or vibrational-rotational transition from the ground state n to the first excited state m. The radiation frequency ω is slightly detuned from the center of the absorption line at ω_{mn}, i.e., $\Omega=\omega-\omega_{mn}$, $(|\Omega|\ll\omega,\omega_{mn})$.

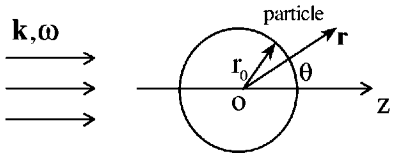

FIG. 1. Geometry of the problem; $\mathbf{k}$ is the wave vector, ω is the frequency of radiation.

Molecules that have absorbed radiation become excited. This alters their transport characteristics and their probability of being captured by the interphase plane. Thus, the gaseous phase can be interpreted as a three-component mixture consisting of the excited and unexcited components of the vapor and the buffer (nonabsorbing and noncondensing) gas. The components of the vapor consist of molecules of equal mass m_1 but different effective diameters $d_n \neq d_m$. As a result of stimulated transitions and the radiative decay of the excited level, these components are constantly swapping molecules.

Resonant interaction between light and vapor destroys the state of phase equilibrium, and evaporation or condensation growth of the aerosol begins. Obviously, the decrease (increase) in particle mass per unit time, i.e., the evaporation (condensation) rate, is determined by the mass vapor flux at the particle's surface,

$$\frac{d}{dt}\left(\frac{4}{3}\pi r_0^3 \rho_0\right) = -2\pi r_0^2 \langle \mathbf{n}\cdot\mathbf{J}\rangle, \tag{1}$$

where ρ_0 is the density of the particle, **n** is the outer normal to the surface of the particle, **J** is the vector of vapor mass flow, the brackets $\langle\cdots\rangle$ indicate the integration over the angle θ (Fig. 1)

$$\langle \mathbf{n}\cdot\mathbf{J}\rangle = \int_0^{\tau} J_r \sin\theta \, d\theta. \tag{2}$$

If the velocity distribution functions of the excited f_m and nonexcited f_n vapor molecules are known, the quantity J_r can be calculated as

$$J_\tau = m_1 \int v_r (f_n + f_m) d\mathbf{v}. \tag{3}$$

When the absorbing molecules are approximated by a two-level model, the velocity distribution functions for the vapor molecules, f_m and f_n, and the molecules of the buffer gas f_2, satisfy the following kinetic equations [3]:

$$\frac{\partial f_n}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla} f_n = \tfrac{1}{2}\Gamma_m \kappa(\mathbf{v})(f_m - f_n) + \Gamma_m f_m + S_n, \tag{4}$$

$$\frac{\partial f_m}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla} f_m = -\tfrac{1}{2}\Gamma_m \kappa(\mathbf{v})(f_m - f_n) - \Gamma_m f_m + S_m, \tag{5}$$

$$\frac{\partial f_2}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla} f_2 = S_2. \tag{6}$$

Here

$$S_i = S_{im} + S_{in} + S_{i2}, \quad i = m,n,2, \tag{7}$$

$$\kappa(\mathbf{v}) = \frac{4|G_{mn}|^2\Gamma}{\Gamma_m[\Gamma^2 + (\Omega - \mathbf{k}\cdot\mathbf{v})^2]}, \quad G_{mn} = \frac{d_{mn}E_0}{2\hbar},$$

where Γ_m is the rate of radiative decay of the excited level, $\kappa(\mathbf{v})$ is the probability of absorption per unit time for molecules with a given velocity **v** (the absorption rate for such molecules), d_{mn} is the dipole matrix element of the m-n transition, E_0 is the amplitude of the electric field of the light wave, G_{mn} is the Rabi frequency, S_{ij} are Boltzmann collision integrals for molecules of the ith and jth species, and $\hbar$ is Planck's constant.

To specify the boundary conditions for Eqs. (4)–(6) we must fix the distribution functions for molecules emitted from the particle surface. Generally, the temperature T_s of the surface differs from the equilibrium temperature T_0, a fact that can be explained either by the absorption of light by the particle or by removal of the latent heat of evaporation. Let us assume that the part α_i, $(i = m,n)$ of the vapor molecules in the ith state is evaporated in an equilibrium manner according to the Maxwell distribution function f_i^s with the surface temperature T_s and with the corresponding number density of saturated vapor n_{is}, and the part $(1-\alpha_i)$ 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_i^r. It is assumed that the function f_i^r depends on the surface temperature T_s and unknown number density n_{1r}. Then ignoring inelastic collisions with the surface, for vapor molecules we have

$$f_i^+(\mathbf{r}_0,\mathbf{v}) = \alpha_i f_i^s + (1-\alpha_i) f_i^r; \tag{8}$$

$$i = m,n; \quad (\mathbf{v}\cdot\mathbf{n}) > 0,$$

where

$$f_i^{s,r} = n_{i(s,r)} \left(\frac{m_1}{2\pi k_B T_s}\right)^{3/2} \exp\left(\frac{m_1 v^2}{2k_B T_s}\right). \tag{9}$$

k_B is the Boltzmann constant.

We assume that molecules of the buffer gas are diffusely scattered by the surface, with their energy being completely accommodated and their velocity distribution function being Maxwellian

$$f_2^+(\mathbf{r}_0,\mathbf{v}) = n_{2r}\left(\frac{m_2}{2\pi k_B T_s}\right)^{3/2} \exp\left(\frac{m_2 v^2}{2k_B T_s}\right) \quad (\mathbf{v}\cdot\mathbf{n}) > 0, \tag{10}$$

where n_{2r} is the number density of the buffer-gas molecules reflected from the surface, m_2 is the mass of a buffer-gas molecule.

Note that all macroscopic quantities in Eqs. (9) and (10) depend on the polar angle θ.

We assume that only unexcited molecules evaporate from the surface. Then in the boundary condition (8) we must put $n_{ms} = 0$, while n_{ns} is the equilibrium density n_s of saturated vapor corresponding to surface temperature T_s.

In expression (9), the unknown number densities n_{ir} of the excited $(i = m)$ and unexcited $(i = n)$ vapor molecules reflected from the surface of the aerosol particle can be found from the balance relations for the mass vapor fluxes at the interphase boundary

$$N_i^+ = (1-\alpha_i)|N_i^{-1}| + \alpha_i N_i^s; \quad i = m,n. \tag{11}$$

Here

$$N_i^{+,s}=\int_{(\mathbf{v}\cdot\mathbf{n})>0} v_r f_i^{+,s}(\mathbf{r}_0,\mathbf{v})d\mathbf{v}. \tag{12}$$

$$|N_i^-|=\int_{(\mathbf{v}\cdot\mathbf{n})<0} |v_r| f_i^{-}(\mathbf{r}_0,\mathbf{v})d\mathbf{v}, \quad N_m^s=0,$$

where the superscripts $+$, $-$, and s refer, respectively, to flows determined by the emitted, incident, and evaporated molecules.

The distribution functions for the emitted f_i^+ and evaporated f_i^s vapor molecules are given by Eqs. (8) and (9), and for the incident molecules f_i^- can be found by solving the Eqs. (4) and (5).

In the boundary condition (10), the unknown number density n_{2r} of reflected buffer-gas molecules can be found from the nonpercolation condition

$$N_2^+=|N_2^-|. \tag{13}$$

The kinetic boundary conditions (8)–(10) include the unknown temperature T_s. The temperature distribution inside the particle T_p and on its surface $T_s=T_p(r_0)$ is described by a nonuniform heat-conductivity equation [6]

$$-\lambda_p \Delta T_p = W(r,\theta), \tag{14}$$

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 according to the Lorenz-Mie theory has the form [6]

$$W(r,\theta)=\frac{4\pi}{\lambda_0} n\chi I B(r,\theta), \quad B(r,\theta)=\frac{|\mathbf{E}(r,\theta)|^2}{E_0^2}. \tag{15}$$

Here n and χ are, respectively, the refractive and absorptive indexes ($N=n+i\chi$ is the complex refraction index), $\mathbf{E}(r,\theta)$ is the local value of the electric field intensity inside the particle, and I is the intensity of radiation; $B(r,0)$ has been averaged over the azimuthal angle φ.

The boundary conditions to the heat-conductivity equation (14) require the temperature limit at the particle center and continuity of radial heat flux on the surface

$$\left(q_r+\frac{L}{m_1}J_r+\lambda_p\frac{\partial T_p}{\partial r}\right)_{r=r_0}=0, \tag{16}$$

where q_r is the radial heat flux in a gaseous phase, and L is the latent heat of phase transition per condensed phase molecule. The second term in Eq. (16) represents the phase transition heat ablation during evaporation, the third one the radial heat flux inside the particle due to the heat conductivity.

The radial heat flux in gaseous phase at the surface of the particle can be calculated as

$$q_r=\sum_{i=m,n,2}\frac{1}{2}m_i\int (v_r-v_{0r})(\mathbf{v}-\mathbf{v}_0)^2 f_i(\mathbf{r}_0,\mathbf{v})d\mathbf{v}. \tag{17}$$

Here $\mathbf{v}_0$ is the mass-average velocity

$$\rho\mathbf{v}_0=\sum_{i=m,n,2} m_i\int \mathbf{v} f_i d\mathbf{v}.$$

$$\rho=n_1m_1+n_2m_2, \quad n_1=n_n+n_m. \tag{18}$$

The radial mass vapor flux at the particle surface taking into account Eqs. (3), (11) and (12) can be calculated as

$$J_r=m_1\sum_{i=m,n}\alpha_i(N_i^s-|N_i^-|). \tag{19}$$

We examine the case of small values of $\kappa(\mathbf{v})$, which is common for vibrational-rotational transitions, while for electronic transitions this case is realized at low light intensities. In this case the state of the system is close to equilibrium and the distribution functions of molecular velocities can be written as perturbed Maxwellian distributions

$$f_i(\mathbf{v})=f_{i0}[1+h_i(\mathbf{v})], \tag{20}$$

$$f_{i0}=n_{i0}\left(\frac{m_i}{2\pi k_B T_0}\right)^{3/2}\exp\left(\frac{m_i v^2}{2k_B T_0}\right),$$

where $h_i(\mathbf{v})$ are the disturbance functions for excited ($i=m$), ground state ($i=n$) and buffer-gas ($i=2$) molecules, n_{i0} is the equilibrium number density of molecules of species i, and T_0 is the equilibrium temperature of the vapor-gas mixture.

The component temperatures differ little from the equilibrium temperature T_0, i.e.,

$$T_i=T_0(1+\tau_i), \quad |\tau_i|\ll 1. \tag{21}$$

where τ_i is the unknown temperature perturbation of the ith component. The equilibrium vapor molecule densities $n_s(T_s)$ and $n_{10}(T_0)$ are also slightly different from one another, i.e.,

$$\nu_s=\frac{n_s-n_{10}}{n_{10}}, \quad |n_s|\ll 1.$$

Then the linearized Clapeyron-Clausius equation [7] has the form

$$\nu_s=(\beta-1)\tau_s, \quad \tau_s=\frac{T_s-T_0}{T_0}, \quad \beta=\frac{L}{k_B T_0}. \tag{22}$$

It follows from the linearity of the theory that the particle evolution can be described independently from the light-induced drift [2] and photophoresis [7,8]. The slow motion of the particle (in linear approximation on the Mach number, i.e., $M\ll 1$) does not influence evaporation rate of this particle.

Consider a quasistationary approximation when the characteristic time of evaporation or growth is much more than the characteristic diffusion (and heat-conductivity) time [1]. In this case the distribution functions do not depend on the time. Then in the kinetic equations (4)–(6) we can ignore the time derivatives of the distribution function.

We consider the free-molecule regime, in which the mean free path of molecules is much greater than the radius of particles. 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 functions of incident molecules are the same as though the particle was absent. If we assume that the intensity of the light is independent of the position and the transverse size of the light beam is much greater than the mean free path of the molecules, the distribution functions f_i^- of the incident molecules are spatially homogeneous. Then in Eqs. (4)–(6), which the functions f_i^- must satisfy, we can ignore spatial derivatives. Note that the full distribution functions depend on coordinates.

We assume that the influence of the "shadow" that the aerosol particle will cast is negligible in the case of the free-molecule regime because only a small part of molecules is in "shaded" area.

Under these assumptions, the linearized variants of Eqs. (4)–(6) for the disturbance functions h_i^∞ at a distance from the particle (for the incident molecules) assume the form

$$\frac{1}{2}\Gamma_m\kappa(\mathbf{v})\left(\frac{n_{n0}}{n_{m0}}-1\right)-\Gamma_m(1+h_m^\infty)+L_{mm}+L_{mn}+L_{m2}=0, \tag{23}$$

$$-\frac{1}{2}\Gamma_m\kappa(\mathbf{v})\left(1-\frac{n_{m0}}{n_{n0}}\right)+\frac{n_{m0}}{n_{n0}}\Gamma_m(1+h_m^\infty)+L_{nm}+L_{nn}+L_{n2}=0, \tag{24}$$

$$L_{2m}+L_{2n}+L_{22}=0. \tag{25}$$

We consider only elastic collisions between molecules, and for the linearized collision integrals L_{ij} we make approximations [9] that ensure accurate values for the first 13 moments of L_{ij}. Obviously, in an approximation linear in $\kappa(\mathbf{v})$ we can assume that $n_m \ll n_n$. Then the solution of Eqs. (23)–(25) takes the form

$$h_m^\infty=\frac{\Gamma_m}{\Gamma_m+\gamma_m}\times\left(\frac{n_{n0}}{2n_{m0}}\kappa(\mathbf{v})-1+\frac{\gamma_m}{\Gamma_m}\nu_m^\infty+\frac{A_m}{\Gamma_m}\right), \tag{26}$$

$$h_m^\infty=\frac{\Gamma_m}{\Gamma_m+\gamma_m}\frac{\gamma_m}{\gamma_n}\times\left[-\frac{1}{2}\kappa(\mathbf{v})+\frac{n_{m0}}{n_{n0}}\left(1+\nu_m^\infty+\frac{A_m}{\gamma_m}\right)\right]+\nu_n^\infty+\frac{A_n}{\gamma_n}, \tag{27}$$

$$h_2^\infty=\nu_2^\infty+\frac{A_2}{\gamma_2}. \tag{28}$$

Here the following designations have been used:

$$A_i=\sum_{j=m,n,2}A_{ij}, \quad \mathbf{c}_i=\frac{\mathbf{v}}{\overline{v}_i}, \quad \overline{v}_i=\left(\frac{2k_BT_0}{m_{i,}}\right)^{1/2}, \tag{29}$$

$$A_{ij}=\left(c_i^2-\frac{3}{2}\right)\left[\gamma_{ij}\tau_i^\infty-2\frac{m_{ij}}{m_j}(\tau_i^\infty-\tau_j^\infty)\nu_{ij}^{(1)}\right],$$

$$\gamma_i=\gamma_{im}+\gamma_{in}+\gamma_{i2}, \quad (i=m,n,2),$$

$$\nu_{ij}^{(1)}=\frac{16}{3}\frac{m_{ij}}{m_i}n_j\Omega_{ij}^{(1,1)}, \quad m_{ij}=\frac{m_im_j}{m_i+m_j},$$

where γ_{ij} is the effective frequency of collisions between the molecules of ith and jth species, $\Omega_{ij}^{(1,1)}$ is the Chapman-Cowling integral [10].

At a distance from the particle, the number density and the temperature disturbances of i species are calculated as

$$\nu_i^\infty=\frac{n_i^\infty-n_{i0}}{n_{i0}}=\pi^{-3/2}\int h_i^\infty\exp(-c_i^2)dc_i, \tag{30}$$

$$\tau_i^\infty=\frac{T_i^\infty-T_0}{T_0}=\pi^{-3/2}\int\left(\frac{2}{3}c_i^2-1\right)h_i^\infty\exp(-c_i^2)d\mathbf{c}_i.$$

Note that generally the expression for A_{ij} in Eq. (29) incorporates terms containing the macroscopic velocities of the vapor and the buffer gas, partial heat fluxes, and components of the stress tensor. However, these terms give a contribution only in a local vapor flow and do not give a contribution to a vapor flow averaged over the surface of the particle.

After linearization of boundary conditions (8)–(10) we obtain the disturbance functions for excited and unexcited vapor molecules and buffer-gas molecules emitted from the surface of the particle

$$h_m^+=(1-\alpha_m)\left[\nu_{\rm mr}+\left(c_1^2-\frac{3}{2}\right)\tau_s\right],$$

$$h_n^+=\alpha_n\nu_s+(1-\alpha_n)\nu_{\rm nr}+\left(c_1^2-\frac{3}{2}\right)\tau_s,$$

$$h_2^+=\nu_{2r}+\left(c_2^2-\frac{3}{2}\right)\tau_s, \quad \nu_{\rm ir}=\frac{n_{1\rm r}-n_{i0}}{n_{i0}}. \tag{31}$$

Here it is taken into account that only unexcited molecules evaporate from the surface. The unknown parameters $\nu_{\rm ir}$ can be found from the Eqs. (11)–(13).

Thus, on the surface of the particle for the disturbance functions we have

$$h_i(\mathbf{r}_0,\mathbf{v})=\begin{cases}h_i^+(\mathbf{r}_0,\mathbf{v}) & (\mathbf{v}\cdot\mathbf{n})>0\\ h_i^\infty(\mathbf{r}_0,\mathbf{v}) & (\mathbf{v}\cdot\mathbf{n})<0.\end{cases} \tag{32}$$

III. RADIAL VAPOR FLUX

In an approximation linear in $\kappa(bfv)$ we have $n_m \ll n_n$, i.e., $n_0 \approx n_1$. Then Eqs. (26) and (30) yield

$$n_m^\infty=n_{m0}(1+\nu_m^\infty)=\frac{n_{10}}{2\pi^{3/2}}\kappa_0, \tag{33}$$

$$\tau_m^\infty=\frac{n_{10}}{2\pi^{3/2}n_{m0}}\frac{\Gamma_m\kappa_2}{\Gamma_m+\nu_{mn}^{(1)}+2\nu_{m2}^{(1)}m_{12}/m_2},$$

where

$$\kappa_0=\int \kappa(\mathbf{v})\exp(-c_1^2)dc_1,$$

$$\kappa_2=\int (c_1^2-\tfrac{3}{2})\kappa(v)\exp(-c_1^2)dc_1. \qquad (34)$$

Both κ_0 and κ_2, which depend on the parameters $x=\Omega/(k\overline{v_1})$ and $y=\Gamma/(k\overline{v_1})$, have a simple form for both inhomogeneous ($y\ll 1$) and homogeneous ($y\gg 1$) line broadening. For intermediate values of *y*, a numerical calculation is carried out in the Appendix.

The relative light-induced cooling (or heating) of the vapor and heating (or cooling) of the buffer gas at a distance from the particle are, respectively,

$$\tau_1^\infty=\frac{n_{20}}{n_{10}+n_{20}}\frac{n_{m0}}{n_{10}}\tau_m^\infty\left(1-\frac{\underline{\Omega}_{2m}^{(1,1)}}{\underline{\Omega}_{2m}^{(1,1)}}\right),$$

$$n_{20}\tau_2^\infty=-n_{10}\tau_1^\infty. \qquad (35)$$

Taking into account Eqs. (2), (12), (19), (20), (26), (27), (31), (33), and (35) for the mass vapor flux integrated over angle 0 we obtain

$$\langle J_r\rangle=G_\tau\langle\tau_s\rangle+\langle J_\kappa\rangle, \qquad (36)$$

where

$$\langle J_\kappa\rangle=\frac{\rho_1\overline{v_1}}{2\pi^{1/2}}\left(G_s\Delta\alpha+G_c\frac{\Delta\gamma}{\gamma_n}+G_T\tau_1^\infty\right), \qquad (37)$$

$$G_\tau=\alpha_n\frac{\rho_1\overline{v_1}}{2\pi^{1/2}}\left(\beta-\frac{1}{2}\right), \quad G_T=\frac{\alpha_n}{2},$$

$$G_s=\frac{\gamma_m}{\Gamma_m+\gamma_m}\frac{\kappa_0}{2\pi^{3/2}}+\frac{\Gamma_m}{\Gamma_m+\gamma_m}\left(\frac{\kappa_1^-}{\pi}+\frac{n_m\nu_{m2}^{(1)}}{2n_1\Gamma_m}\frac{m_1-m_2}{m_1+m_2}\tau_m^\infty\right), \qquad (38)$$

$$G_c=\frac{\alpha_n\Gamma_m}{\Gamma_m+\gamma_m}\left(\frac{\kappa_0}{2\pi^{3/2}}-\frac{\kappa_1^-}{\pi}-\frac{\kappa_2}{6\pi^{3/2}}\right), \qquad (39)$$

$$\kappa_1^-=\frac{1}{2}\int_0^\pi \sin\theta\, d\theta\int_{c_{1r}<0}|c_{1r}|\kappa(\mathbf{v})\exp(-c_1^2)d\mathbf{c}_1,$$

$$\Delta\alpha=\alpha_0-\alpha_m, \quad \Delta\gamma=\gamma_n-\gamma_m, \quad \rho_1=m_1n_1. \qquad (40)$$

The quantity κ_1^- is given as a function of parameters *x,y* in the Appendix.

In Eq. (36), the kinetic coefficient G_τ characterizes the radiative evaporation of an aerosol particle. In Eq. (37) the coefficient G_s characterizes the surface mechanism of evaporation (or growth), which is related to the difference in the evaporation-condensation coefficients for the excited and unexcited vapor molecules. The kinetic coefficient G_c characterizes the contribution related to the difference in rates of collisions of the excited and unexcited vapor molecules. Finally, the third term in Eq. (37) describes the rate of condensation growth (or evaporation) of the aerosol particle due to light-induced cooling (or heating) of the vapor.

For calculation the quantity $\langle\tau_s\rangle$ in Eq. (36) it is necessary to determine the radial heat flux. From Eq. (17) integrating over the angle θ we obtain

$$\langle q_r\rangle=Q_\tau\langle\tau_s\rangle+\langle q_\kappa\rangle. \qquad (41)$$

Here

$$Q_\tau=p_1\overline{v_1}\left[\alpha_n\frac{(\beta-1)}{\pi^{1/2}}+\pi^{-1/2}\left(1+\frac{\alpha_n}{2}\right)+\frac{n_{20}}{n_{10}}\left(\frac{m_1}{m_2}\right)^{3/2}\right], \qquad (42)$$

$$\langle q_\kappa\rangle=p_1\overline{v_1}\left(Q_s\Delta\alpha+Q_c\frac{\Delta\gamma}{\gamma_n}+Q_T\tau_1^\infty\right), \qquad (43)$$

where

$$Q_s=\frac{\pi^{-1/2}\Gamma_m}{\Gamma_m+\gamma_m}\left(\frac{\kappa_1^-}{\pi}-\frac{\kappa_0}{2\pi^{3/2}}\right.$$
$$\left.+\frac{m_2-m_1}{m_2+m_1}\frac{\nu_{m2}^{(1)}}{\Gamma_m+\nu_{mn}^{(1)}+2(m_{12}/m_2)\nu_{m2}^{(1)}}\frac{\kappa_2}{6\pi^{3/2}}\right), \qquad (44)$$

$$Q_c=\frac{\pi^{-1/2}\Gamma_m}{\Gamma_m+\nu_{mn}^{(1)}+2(m_{12}/m_2)\nu_{m2}^{(1)}}\frac{\kappa_2}{2\pi^{3/2}}+\frac{\pi^{-1/2}\Gamma_m}{\Gamma_m+\gamma_m}$$
$$\times\left[(1-\alpha_n)\left(\frac{\kappa_1^{-1}}{\pi}-\frac{\kappa_2}{6\pi^{3/2}}\right)+\alpha_n\frac{\kappa_0}{2\pi^{3/2}}+\frac{\kappa_3^-}{2\pi}\right], \qquad (45)$$

$$Q_T=\frac{1}{2\pi^{1/2}}\left[\left(\frac{m_1}{m_2}\right)^{1/2}-1-\alpha_n\right], \qquad (46)$$

$$\kappa_3^-=\frac{1}{2}\int_0^\pi \sin\theta d\theta\int_{c_{1r}<0}c_{1r}^2|c_{1r}|\times\kappa(\mathbf{v})\exp(-c_1^2)d\mathbf{c}_1; \qquad (47)$$

p_1 is the vapor pressure at the equilibrium temperature T_0, the quantity κ_3^- is given as a function of parameters *x*, *y* in the Appendix.

The solution of heat-conductivity equation (14) together with boundary condition (16) gives [11]

$$\langle\tau_s\rangle=\frac{\Phi_0-\Psi_0}{Q_\tau+LG_\tau}, \quad \Phi_0=\tfrac{1}{4}IK_a, \qquad (48)$$

$$\psi_0=\langle q_\kappa\rangle+L\langle J_\kappa\rangle,$$

$$K_a=4\rho_0n\chi\int_0^\pi \sin\theta\, d\theta\int_0^1 s^2B(s,\theta)ds,$$

$$s=\frac{r}{r_0}, \quad \rho_0=\frac{2\pi r_0}{\lambda_0}.$$

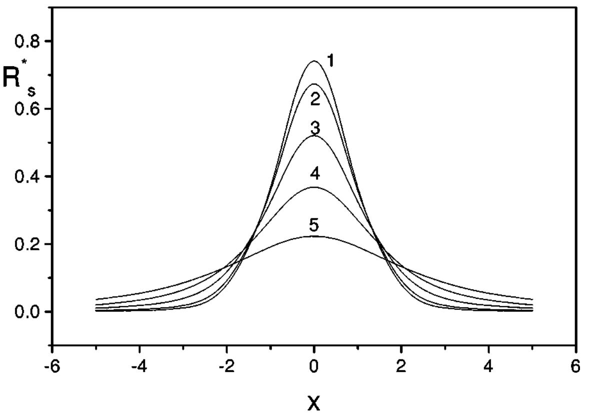

FIG. 2. Kinetic coefficient R_s^* [Eq. (52)] as a function of the detuning parameter $x=\Omega/(k\overline{v}_1)$ and homogeneous broadening parameter $y=\Gamma/(k\overline{v}_1)$; $y=0.1$ (curve 1), 0.2 (curve 2), 0.5 (curve 3), 1 (curve 4), and 2 (curve 5).

Here function $B(s,\theta)$ is given in Eq. (15), ρ_0 is the diffraction parameter. The calculation of efficiency factor K_a of the radiation absorption by the particle on the basis of Lorenz-Mie theory has been given in Ref. [12].

Thus Eq. (36) is transformed into the following form:

$$\langle J_r\rangle = R_r\frac{m_1}{L}\Phi_0 + \frac{\rho_1\overline{v}_1}{2\pi^{1/2}}\left(R_s\Delta\alpha + R_c\frac{\Delta\gamma}{\gamma_n} + R_T\tau_1^{\infty}\right), \tag{49}$$

where

$$R_\tau = \frac{LG_\tau}{Q_\tau m_1 + LG_\tau}, \quad \eta = \frac{m_1 Q_\tau}{Q_\tau m_1 + LG_\tau}, \tag{50}$$

$$R_k = \eta G_k - \frac{2\pi^{1/2}}{\beta}(1-\eta)Q_k, \quad k=s,c,T.$$

The kinetic coefficients G_k, Q_k are given by Eqs. (37)–(39), (42), and (44)–(46).

Thus there are four mechanisms of evolution of the aerosol particle: radiative evaporation R_r, surface R_s, collisional R_c, and temperature R_T evolution.

In the case of pure vapor ($n_2=0$) for typical condition $\beta \gg 1$ we obtain

$$R_\tau = 1, \quad R_s = \frac{\kappa_0}{\pi^{3/2}\beta}, \quad R_c = -\frac{2}{\beta}\frac{\Gamma_m}{\Gamma_m+\gamma_m}\left(\frac{\kappa_1^-}{\pi} + \frac{\kappa_3^-}{2\pi} + (1+\alpha_n)\frac{\kappa_2}{3\pi^{3/2}}\right). \tag{51}$$

In pure vapor the temperature mechanism is absent because $\tau_1^{\infty}=0$ (the light-induced cooling or heating of the vapor takes place only in the presence of the buffer gas).

The modified kinetic coefficients R_s^* and R_c^* for pure vapor as a function of the parameter $x=\Omega/(k\overline{v}_1)$ are shown in Figs. 2 and 3. With the preceding notation we have

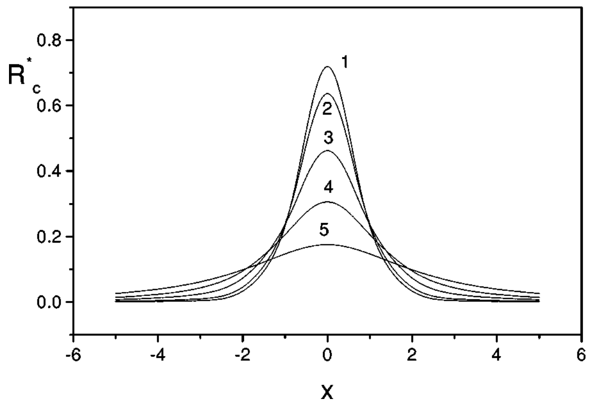

FIG. 3. Kinetic coefficient R_c^* (eq. (52)) as a function of detuning parameter $x=\Omega/(k\overline{v}_1)$ and homogeneous broadening parameter $y=\Gamma/(k\overline{v}_1)$; $y=0.1$ (curve 1), 0.2 (curve 2), 0.5 (curve 3), 1 (curve 4), and 2 (curve 5).

$$R_s^* = \frac{\Gamma_m k\overline{v}_1\beta}{8G_{mn}^2}R_s, \tag{52}$$

$$R_c^* = \frac{(\Gamma_m+\gamma_m)k\overline{v}_1\beta}{8G_{mn}^2}R_c.$$

If we choose effective rates of collisions of the i-j in the form $\gamma_{ij}=\nu_{ij}^{(1)}$ and assume that the interacting molecules are hard elastic spheres and that the effective interaction radii of excited d_{m2} and ground state d_{n2} vapor molecules with the buffer-gas molecules are commensurate, i.e., $|d_{n2}-d_{m2}|/d_{n2} \ll 1$, the expression (49) for the mass-average flux of the vapor becomes

$$\langle J_r\rangle = R_\tau\frac{m_1}{L}\Phi_0 + \frac{\rho_1\overline{v}_1}{2\pi^{1/2}}\left(R_s\Delta\alpha + R_d\frac{\Delta d}{d_{n2}}\right). \tag{53}$$

Here

$$d_{ij} = \tfrac{1}{2}\langle d_i + d_j\rangle, \quad \Delta d = d_{n2} - d_{m2}, \tag{54}$$

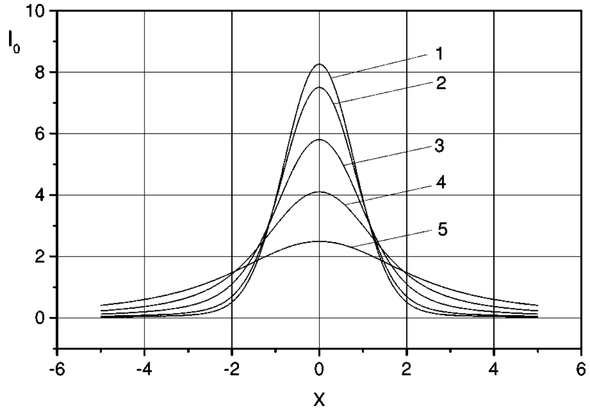

FIG. 4. I_0 as a function of detuning parameter x for various values of homogeneous broadening parameter $y=0.1$ (curve 1), 0.2 (curve 2), 0.5 (curve 3), 1 (curve 4), and 2 (curve 5).

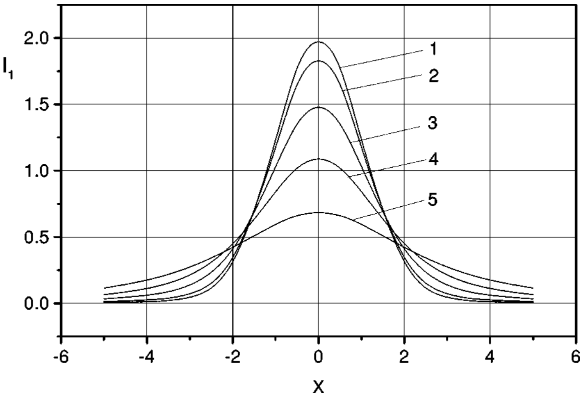

FIG. 5. I_1 as a function of detuning parameter x for various values of homogeneous broadening parameter $y=0.1$ (curve 1), 0.2 (curve 2), 0.5 (curve 3), 1 (curve 4), and 2 (curve 5).

$$R_d = 2\tau_m^{\infty} \frac{n_{m0}}{n_{10}} \frac{n_{20}}{n_{10}+n_{20}} R_T + 2\xi R_c ,$$

$$\xi = \frac{(m_1/2)^{1/2} n_{10} d_n d_{n2} + m_{12}^{1/2} n_{20} d_{n2}^2}{(m_1/2)^{1/2} n_{10} d_n^2 + m_{12}^{1/2} n_{20} d_{n2}^2}.$$

The coefficients R_r and R_s are the same as in Eq. (50).

The second term in parentheses in Eq. (53) characterizes the bulk mechanism of evaporation (or growth) of the particle, a mechanism related to the transport properties of the excited and unexcited vapor molecules.

IV. DISCUSSION

The kinetic coefficients R_s and R_d, which characterize the surface and bulk evaporation (or condensation growth) mechanisms of an aerosol particle, are proportional to the radiation intensity and depend on the ratio of the rate of radiative decay of an excited level Γ_m to the intermolecular collision rate γ_m. The value of Γ_m/γ_m, which depends on gas pressure, has a stronger effect on the bulk component of the radial vapor flux.

The rate of particle evaporation or growth is strongly dependent on the magnitude of the detuning Ω of the radiation frequency from the center of the absorption line of vapor molecules. In contrast to the phenomenon of light-induced drift, [2] the direction of the radial vapor flux is independent of the sign of Ω, i.e., the kinetic coefficients R_s and R_d are even functions of Ω. Here the evaporation (or growth) rate peaks at exact resonance, $\Omega=0$.

The magnitude of the detuning Ω determines the light-induced cooling or heating of the vapor, i.e., the sign of relative variation of the vapor temperature τ_1^{∞}. From Eqs. (35) and (33) we see that the sign of τ_1^{∞} is determined by the signs of Δd and κ_2. Suppose that the effective diameter of molecules that have absorbed light increases $(\Delta d<0)$. Then as Fig. 6 shows, for small values of Ω the vapor heats up, while for large values of Ω it cools off. Thus, there exists an inversion value Ω_{inv} that depends on the parameter $y=\Gamma/(k\overline{v_1})$. For inhomogeneous broadening $(y\ll 1)$, $\Omega_{\mathrm{inv}}\approx 7.5\Gamma$, while for $y=2$ we have $\Omega_{\mathrm{inv}}\approx 0.751$. When $\Delta d<0$, the third term in square brackets on the right-hand side of the Eq. (37) for the radial vapor flux describes evaporation of a particle if $\Omega<\Omega_{\mathrm{inv}}$ and condensation growth if $\Omega>\Omega_{\mathrm{inv}}$.

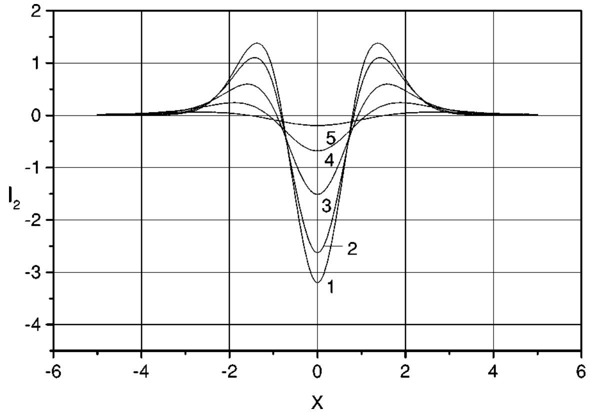

FIG. 6. I_2 as a function of detuning parameter x for various values of homogeneous broadening parameter $y=0.1$ (curve 1), 0.2 (curve 2), 0.5 (curve 3), 1 (curve 4), and 2 (curve 5).

The kinetic coefficient R_s is always positive. Therefore, the surface mechanism gives evaporation of the particle at $\Delta\alpha>0$ and condensation growth at $\Delta\alpha<0$. As to coefficient R_d, it can be both positive and negative depending on concrete requirements. If the concentrations of the vapor and buffer gas are approximately identical $(n_{10}\approx n_{20})$ or the buffer gas misses $(n_{20}=0)$, the kinetic coefficient R_d is plus. In case of small concentration of the vapor $(n_{10}\ll n_{20})$ the coefficient R_d changes the sign at the inversion value of detuning, $\Omega=\Omega_{\mathrm{inv}}$. Thus at $n_{10}\ll n_{20}$ the bulk mechanism gives evaporation or condensation growth of the particle depending on the signs of Δd and $(\Omega-\Omega_{\mathrm{inv}})$.

We now make some numerical estimates for a specific system under typical experimental conditions. We take a sodium particle whose radius r_0 is 1 μm and immerse it in a mixture of sodium vapor and the inert gas argon at temperature T_0 equal to 700 K. The saturated vapor pressure is 306 Pa. The effect of surface curvature can be neglected. Consider the equimolar mixture: $n_{10}=n_{20}\approx 3\times 10^{22}$ m^{-3}. The molecular characteristics are

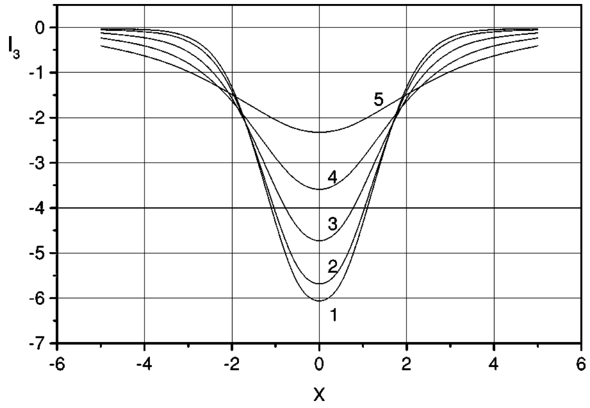

FIG. 7. I_3 as a function of detuning parameter x for various values of homogeneous broadening parameter $y=0.1$ (curve 1), 0.2 (curve 2), 0.5 (curve 3), 1 (curve 4), and 2 (curve 5).

$$m_1 = 3.82\times10^{-26}\ \text{kg},\quad m_2 = 2.6\times10^{-26}\ \text{kg},$$

$$d_1 = 3.0\ \text{Å},\quad d_2 = 3.4\ \text{Å}.$$

The source of light is a tunable dye laser emitting in the vicinity in the D_1 and D_2 lines of sodium (wave length $\lambda_0 \approx 600\,\text{nm}$). The radiated power is about 10 mW and the beam diameter is about 1 mm. At this intensity the Rabi frequency G_{mn} [see Eq. (7)] is of order 10^8 Hz. The radiative decay rate $\Gamma_m \approx 6\times10^7$ Hz [13]. Finally, the parameter $y = 0.01$ corresponds to inhomogeneous line broadening. It can be shown that the refractive, n, and absorptive, χ, indexes of the particle are equal to 0.00 and 2.62, respectively. Then an efficiency factor K_a of the radiation absorption by the particle is equal to 0.00, i.e., the temperature T_s of the surface differs from the equilibrium temperature T_0, a fact that can be explained only by the latent heat of phase transition.

The calculation gives that the Knudsen number (Kn) is approximately 100, which corresponds to the free-molecule regime, and $\beta = 17.1$, $\tau_1^\infty = 1.98\times10^{-4}$. For the kinetic coefficients we obtain

$$R_s \approx 0.007,\quad R_c \approx 0.004,\quad R_T \approx 0.11.$$

If we assume that $\Delta\alpha = 0.01$ and $\Delta d/d_{n2} = 0.01$, then $\langle J_r\rangle \approx 3\times10^{-5}\ \text{kg}\,\text{m}^{-2}\ \text{s}^{-1}$, i.e., the particle loses approximately $4\times10^{-16}\,\text{kg}\,\text{s}^{-1}$. As the mass of particle is 4×10^{-15} kg, the evaporation time is approximately 10 s.

In conclusion, we note that experimental study of this problem at a variety of buffer-gas pressures and values of Ω might become a source of accurate information about evaporation-condensation coefficients and transport characteristics of excited molecules.

ACKNOWLEDGMENTS

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APPENDIX

Here we find the dependence of κ_0, κ_1^-, κ_2 and κ_3^- on the parameters $x = \Omega/(k\overline{v}_1)$ and $y = \Gamma/(k\overline{v}_1)$. It is convenient to write

$$\kappa_0 = \frac{4G_{mn}^2}{\Gamma_m k\overline{v}_1} I_0(x,y),\quad \kappa_1^- = \frac{4G_{mn}^2}{\Gamma_m k\overline{v}_1} I_1(x,y), \tag{A1}$$

$$\kappa_2 = \frac{4G_{mn}^2}{\Gamma_m k\overline{v}_1} I_2(x,y),\quad \kappa_3^- = \frac{4G_{mn}^2}{\Gamma_m k\overline{v}_1} I_3(x,y).$$

The results of numerical calculation for various values of the parameters x and y are plotted in Figs. 4–7.

For inhomogeneous broadening $(y \ll 1)$ with $x \ll 1$ we have

$$I_0 = \pi^2,\quad I_1 = \frac{\pi^{3/2}}{3},\quad I_2 = -\frac{\pi^2}{2},\quad I_3 = \frac{\pi^{3/2}}{2}. \tag{A2}$$

For homogeneous broadening $(y \gg 1)$ with $(x < y)$ we have, to within terms of order y^{-1},

$$I_0 = \frac{\pi^{3/2}}{y},\quad I_1 = \frac{\pi}{2y},\quad I_2 = 0,\quad I_3 = -\frac{\pi}{y}. \tag{A3}$$

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