ELECTROMAGNETIC CONTROL OF THE DIFFUSION INTERACTION OF AEROSOL DROPLETS

I. E. Nakhutin, P. P. Poluéktov,
and A. N. Semykin

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The diffusion mechanism of interaction between evaporating and condensing droplets is discussed. It is found that the resulting forces are of long-range type. The scope for using resonant electromagnetic radiation to act on the growth or evaporation of the droplets is also discussed.

Experiment shows [1] (see also [2]) that small aerosol particles are repelled by evaporating droplets and attracted by growing ones. The results were explained qualitatively as the action of hydrodynamic flows arising around the evaporating or condensing drops (the flow directions in evaporation and condensation are opposite). Stefan [2] explained the causes of this motion in a vapor–gas mixture: in order to maintain a constant total pressure in the medium, the gradient in the partial pressure of the vapor (arising from the diffusion during evaporation and condensation) must be accompanied by an equal gradient of opposite direction in the partial pressure of the gas, which causes the gas to diffuse towards the particle, but the latter is impermeable, so the gas flow at it should be zero, and therefore one gets hydrodynamic Stefan flow, which compensates for the gas diffusion. Therefore, the primary reason for the flow near a drop is the diffusion of vapor into the gas, and therefore this droplet interaction mechanism should be called a diffusion one. This enables one to distinguish this interaction from the hydrodynamic one between particles, which arises when particles of a nonvolatile material move in a medium.

However, no quantitative study has been made of the diffusion interaction and of its effects on fog stability. It is shown below that very considerable forces act in an ensemble of volatile particles, which are inversely proportional to the square of the distance between the particles, which means that the interaction is of long-range type (similar to the Coulomb one). For comparison, we may note that Van der Waals' forces decrease as r^{-7} [2], while hydrodynamic interaction ones decrease as r^{-5} [2]. We have also found that the diffusion mechanism can be controlled if the electromagnetic radiation acts on the aerosol system that is reasonantly absorbed by the vapor. The action of the radiation in that case is of two types: firstly, the diffusion coefficients in the ground and excited states differ, and secondly there are differences in the condensation (evaporation) coefficients that characterize the probability that vapor atoms will stick to the surface of a particle. The effects of these factors are very substantial: it is quite possible to get a situation where droplets that are evaporating and consequently repel one another by the diffusion mechanism on illumination grow and attract one another, which may ultimately lead to coalescence in the aerosol cloud.

Diffusion Interaction of Droplets Suspended in a Foreign Gas. Evaporation or condensation at the droplets is accompanied by Stefan hydrodynamic flows, which are found by joint solution of the equations of diffusion, thermal conduction, and hydrodynamics. For simplicity we restrict ourselves to the case where the concentration of vapor atoms is small by comparison with that of the surrounding buffer gas. For the vapor close to saturation we get [2] that in the linear approximation near a drop of radius R the radial velocity of the Stefan flow is

$$\vec{v}_1 = v\frac{R^2}{r^2}\vec{n}_1, \quad v = \frac{D}{R_1}\frac{n_s(R_1) - n_\infty}{n_0}. \tag{1}$$

The unit vector $\vec{n}_1$ is directed away from the surface of the drop. The solution of (1) may be refined in many respects (by the inclusion of thermal and nonlinear effects, the recoil momentum of the escaping molecules, etc.), but to a first approximation it is sufficient to use (1). If there is a spherical particle of radius R_2 at a distance r from a drop of radius R_1, then the former is acted on by the Stokes force

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$$\vec{F}_{21} = 6\pi\eta R_2 \vec{v}_1(r), \tag{2}$$

where η is the viscosity of the surrounding medium. The use of this formula involves the assumption that $r \gg R_1, R_2$, since the speed of the hydrodynamic flow is considered as constant in the neighborhood of the second particle, and also no allowance is made for the distortion in the gas flow due to the adjacent particle.

If the two particles are drops of the same substance, then we find within the accuracy of the linear approximation that the forces acting on the different particles are described by the latter formula with corresponding permutation of the subscripts. On the basis of (1) we see that the interaction between the droplets occurs with forces inversely proportional to the square of the distance between them, which is similar to the forces between electric charges. However, the analogy is not complete. An important point is that the forces $\vec{F}_{12}$ and $\vec{F}_{21}$ in the general case are not equal in modulus and even may have the same direction, because a third body (the vapor) is involved in the interaction. In fact, if the saturation-vapor pressure were independent of the droplet size, then the forces $\vec{F}_{12}$ and $\vec{F}_{21}$ would be identical in magnitude and opposite in direction, but according to Kelvin's formula [2]

$$n_s(R) - n_s(\infty) = n_s(\infty)\frac{2\sigma m}{\gamma kT} R^{-1},$$

the saturation vapor pressure over the surface of a drop increases as the size decreases. If we have two drops differing in size and one of them evaporates while the other grows (i.e., the saturation-vapor concentration satisfies the chain of inequalities $n_S(R_1) > n_\infty > n_S(R_2)$ $(R_1 < R_2)$) then the forces $\vec{F}_{12}$ and $\vec{F}_{21}$ are the same in direction, and the small drop follows the large one. Therefore, there is an apparent violation of Newton's third law because of the participation of a third body in the interaction. Refinement of the formulation and derivation of the solution (for example, with allowance for the recoil of the evaporating material) only strengthens this conclusion; we note however, that in any case the forces $\vec{F}_{12}$ and $\vec{F}_{21}$ are equal in modulus and opposite in sign if the drops are of the same size, where the evaporating drop is repelled, while on condensation on the other hand it is attracted. The statement relates to drops of the same substance. If, on the other hand, the liquids are different, then the forces are unequal even for equal sizes.

We now estimate the magnitude of the interaction. Consider, for example, two drops of water with radii $R_1 = R_2 = 10\ \mu m$ at a distance $r = 100\ \mu m$ apart in air at room temperature ($T = 290°K$), where the saturation vapor pressure is 0.02 atm [3]. With a humidity of 99%, repulsive forces $F_{12} = F_{21} = 3 \cdot 10^{-9}$ dyn act between the drops, which coincide with the weights of these drops. Therefore, the diffusion forces are very substantial and evidently may make a definite contribution for example to the kinetics of aerosol coaleasence.

To conclude this section we make the following comments. We have discussed above the stationary case of flow and diffusion, and therefore the applicability of the results is restricted to the following: the particles must be moving with respect to the air with speeds less than the speeds of the hydrodynamic flows, while the evaporation (condensation) times must be much greater than the characteristic hydrodynamic and diffusion times: $\tau_{hd} \sim \rho_0 r^2/\eta$, $\tau_d \sim r^2/D$.

Control of Droplet Growth and Evaporation by Means of Resonant Laser Radiation. Before we consider the scope for affecting the growth and evaporation, we recall how these processes are described in the absence of radiation. For this purpose we solve the diffusion equation $\Delta n = 0$ with the following boundary conditions: the vapor is saturated at the surface of the body, while far from the body the vapor concentration is n_∞. The rate of growth (evaporation) is determined by the mass flux per unit area, which is $D(\partial n/\partial r)$ (the direction towards the surface is taken as positive). An important point is that the saturation condition corresponds to the flux of molecules from the surface being equal to the number of molecules that attach to the surface, which in turn is equal to the flux of molecules colliding with the surface multiplied by the condensation coefficient. This means that if this coefficient is variable the product by the saturation vapor pressure remains constant.

We now consider whether external fields can be used to affect the growth or evaporation. Let the vapor – gas mixture be in the field of monochromatic electromagnetic radiation that is reasonantly absorbed by the vapor molecules. We assume that the radiation line is broad enough to excite all the molecules within the absorption line: in that case there are no light-induced drift fluxes [4]. The excited vapor molecules interact with the molecules in the environment in a different way from those in the ground state, which occurs on the one hand in that excited molecules have diffusion coefficients different from those in the ground state (because the collisional frequencies of molecules in different states differ substantially [4]). On the other hand, the surface binding forces differ for molecules in the excited and ground states, so the condensation coefficient should change substantially on excitation [5], evidently as far as values of one (in the ground state, the coefficient is extremely small: for example, for pure water $\alpha = 0.034$ [2]).

Therefore, the altered diffusion and condensation coefficients for the excited molecules open up scope for controlling the growth or evaporation. The problem is formulated mathematically as follows. The ground and excited states of the molecule are denoted by subscripts n and m correspondingly, and the vapor diffusion is described by

$$D_n \Delta n_n + D_m \Delta n_m = 0. \tag{3}$$

The differences between the condensation coefficients in the different states are incorporated to write the boundary condition at the surface as

$$\alpha_n n_n + \alpha_m n_m = \alpha_n n_s, \tag{4}$$

where n_s is the saturation-vapor density near the surface in the absence of the external field. The condition at infinity remains unchanged. In the resonant field, the concentrations of the molecules in the ground and excited states are expressed in terms of n (the concentration of molecules at a given point) as follows [6]: $n_n + n_m = n$, $n_m = (1/2)\varkappa/(1+\varkappa)n$, where the saturation parameter is $\varkappa = (2\pi c^2/\hbar\omega^3\Omega)I_\omega$, in which c and $\hbar$ are the velocity of light and Planck's constant, ω and I_ω are the frequency and spectral density of the incident radiation, and Ω is the transition-line half width.

The radiation has another effect apart from exciting the vapor molecules that determines the growth or evaporation: the particles are heated, which firstly increases the saturation vapor density near the surface and secondly produces thermal diffusion. If we restrict ourselves to the case of low vapor concentration, the nonlinear [7] thermal diffusion of the vapor can be neglected.

Therefore, examination of the growth or evaporation in a resonant radiation field requires joint solution of the diffusion equation (3), Maxwell's equations for the field near the surface, and the equation of thermal conduction.

We consider how the excitation and heating affect the evaporation (condensation) when one can neglect the distortion of the field by a particle (this is so if the absorption length for the massive liquid is much greater than the droplet size, and also if the optical density of a droplet is $\varepsilon - 1 \ll 1$, the latter condition sufficient at least when the particle radius does not exceed a few wavelengths [8], with ε the dielectric constant of the particle material). As the heat power produced in unit volume is [9] $q = [9\varepsilon''/(\varepsilon' + 2)^2 + \varepsilon''^2]I\omega/c$ (ε' and ε'' are the real and imaginary parts of the dielectric constant, c is the velocity of light, and I is incident radiation intensity), we get from the equation of thermal conduction that the particle temperature is $T = T_\infty + qR_1^2/3\varkappa_l$, where R_1 is particle radius and $\varkappa_l$ is the thermal conductivity outside the particle (we have incorporated the fact that usually $\varkappa_l \ll \varkappa_i$, where the subscript l relates to the material of the particle). In accordance with (3), the vapor density varies in space as follows: $n = n_\infty + A(R_1/r)$, where A is found from boundary condition (4):

$$A = \frac{1}{1 + \frac{\alpha_m - \alpha_n}{2\alpha_n}\frac{\varkappa}{1+\varkappa}} n_s \left(T_\infty + \frac{qR_1^2}{3\varkappa_l}\right) - n_\infty. \tag{5}$$

In the limit where the transition is saturated ($\varkappa > 1$) (5) simplifies to

$$A = \frac{2\alpha_n}{\alpha_m - \alpha_n} n_s \left(T_\infty + \frac{qR_1^2}{3\varkappa_l}\right) - n_\infty. \tag{5'}$$

According to (3), the following is the effective diffusion coefficient when we can neglect the distortion of the external field outside the particle

$$D = D_n \frac{1 + \frac{1}{2}\varkappa}{1+\varkappa} + D_m \frac{\frac{1}{2}\varkappa}{1+\varkappa}, \tag{6}$$

while the vapor flux from unit surface of the particle is

$$j = -D\frac{\partial n}{\partial r} = DAR_1. \tag{7}$$

Then if A is positive the drop evaporates, while otherwise it grows. Formulas (5) and (5') show that it is quite possible to have a situation where a drop evaporating in the absence of the field begins to grow in response to the resonant radiation, which means that although $n_s(T_\infty) - n_\infty > 0$ it is possible in the case $\alpha_m > \alpha_n$ to have $A(\varkappa) < 0$.

There is difficulty in carrying out the necessary estimates because of the indefiniteness of our information on the change in the condensation coefficient on excitation. Even if we assume that α_m is only twice α_n, we find from the data of [3] that at room temperature with a relative humidity of 99% an infrared radiation field with $I \simeq 1$ W/cm^2 will cause water drops of radius less than 4 μm to grow, while ones larger than 4 μm evaporate, which means that on irradiating a dispersed aerosol cloud, all the particles tend to have the same size defined by the condition $A = 0$. Consideration of the kinetics in that case would be of independent interest. In a dense aerosol cloud, clearly an important part will be played by the coalescence of the growing drops arising from the diffusion interaction (and also because of collisions between drops), and rain will be produced.

Therefore, very considerable diffusion-interaction forces act between droplets in clouds (or between solid particles of volatile substances), which arise only from the diffusion of vapor to or from a particle. An illustration of the difference of these forces from others (hydrodynamic, Van der Waals', and so on) is that they become zero in the absence of growth or evaporation. An important point is that these are long-range forces inversely proportional to the square of the distance. The participation of a third body (the vapor) means that there is an apparent violation of Newton's third law in droplet interaction. There is an analogy between these forces and the interaction between drops in an electron-hole liquid in a semiconductor via the phonon wind [10], and also an analogy with the diffusion interaction between damage pores in crystals irradiated by neutrons in a reactor [11].

It is thus possible to control the growth or evaporation of droplets by applying resonant electromagnetic radiation to the vapor. Here we can draw a parallel with the action of resonant laser radiation on phase transitions of gas–liquid type [5]. The scope for controlling the droplet size is at the same time scope for controlling the interaction between them. External fields also produce specific interactions between droplets: rapidly decreasing dipole–dipole ones and also the dynamic Coulomb effect when the photoelectric effect is produced at the surfaces, but these can occur only under special conditions.

Some interest also attaches to the above possibility of making a monodisperse aerosol by acting on a fog.

NOTATION

r, distance between particles; R_1, R_2, radii of particles 1 and 2; n_0, buffer gas density; n_∞, vapor density far from a drop; $n_s(R_1)$, $n_s(\infty)$, density of saturated vapor near a drop of radius R_1 and a flat surface; D, diffusion coefficient in buffer gas; σ, γ, surface tension and density of liquid; m, molecular mass of liquid; k, Boltzmann's constant; T, temperature; ω, I, frequency and intensity of electromagnetic radiation; ε, ε', ε'', dielectric constant of a particle, real and imaginary parts; c, velocity of light.

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