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On the problem of evaporation of water droplets under the action of light irradiation

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Abstract

According to experimental data, irradiation of water droplets accelerates the evaporation process. In this paper, we propose a model that considers the influence of non-equilibrium molecular vibrations created by the radiation on the evaporation rate. The excited molecules transform their vibration energy into energy of translational motion while colliding with the droplet surface and increase the effective evaporation rate. The theoretical results are in qualitative agreement with the experimental data.

Evaporation of liquid droplets in different atmospheres is still of great importance in many technological processes and in ecology. Evaporation under the action of laser radiation has inspired renewed interest in this issue [1]. Increase in the evaporation rate under the action of electromagnetic radiation is usually associated with heating of the droplet surface which stimulates acceleration of the evaporation [2].

However, it has been found experimentally [3], when studying the evaporation of water droplets irradiated by the light of a quartz–halogen bulb and in the dark regime (with no irradiation), that the corresponding curves of evaporation rates versus inverted pressure $1/p$ at comparatively high pressures practically coincide. They slowly diverge with decreasing pressure. At the same time, there were no noticeable variations in the droplet temperature under the action of light.

In this paper, we propose one more mechanism that may result in an increase in the evaporation rate of liquid droplets caused by the interaction of vibration excited molecules of the vapour with the droplet surface. The excited vapour molecules are caused by the light.

In heterogeneous gas systems consisting of some amount of non-equilibrium vibration excited molecules and some disperse inclusions (liquid droplets, solid granules), relaxation of the vibration energy may occur in intermolecular collisions in the bulk or in collisions of the vibration excited molecules with the surface. In these processes the non-equilibrium vibration energy of excited molecules may transform into the energy of kinetic degrees of freedom. These processes are called the bulk and the surface $V-T$ relaxation processes respectively. As a result of the surface $V-T$ relaxation, the molecular vibration energy redistributes between the surface

collective vibrations and the energy of translational motion of the molecule. Probabilities of the surface V - T relaxation of diatomic symmetrical molecules were calculated in [4]. In particular, for typical conditions of evaporation processes, the probability of transition of a molecule from the first excited state to the ground state in one collision with the surface w_{10}^s is given by the expression

$$w_{10}^s = \pi^2 \left(\frac{2}{3}\right)^{3/2} \frac{M\omega_0 a^2}{\hbar} \alpha^{1/2} e^{-\alpha}, \quad (1)$$

v with index T is the molecule thermal velocity where M is the mass of the molecule, ω_0 is the frequency of the molecular vibrations, a is a typical length of the surface–molecule interaction, v_T is the molecule thermal velocity, $\alpha = 3(\pi\omega_0 a/v_T)^{2/3}$. The probability of the bulk V - T relaxation (collision between a vibration excited state and a non-excited state with removal of the vibration quanta) according to Landau and Teller may be written in the form (see, for example, [5])

$$w_{10}^b = \frac{A}{T^{1/6}} e^{C/T^{1/3}}, \quad (2)$$

where A and C are some constants. It is interesting to note that the temperature dependence in (1) is the same as that in (2).

Usually, typical frequencies of the molecular vibrations are much larger than the limiting frequencies of the surface collective vibrations. Therefore, only a negligible part of the vibration quanta may be transferred to the surface oscillators. In other words, the vibration excited molecule coming to the surface with the heat velocity v_T after de-excitation ‘jumps’ with a velocity

$$v = v_T \left(1 + \frac{2\hbar\omega_0}{Mv_T^2}\right)^{1/2}. \quad (3)$$

However, the probability of this event in one collision at normal conditions is extremely small. This becomes obvious upon substituting numerical values of typical parameters in (1) and setting a to be of the order of the amplitude of the molecular vibrations (10^{-8} cm).

In fact, de-excitation of molecules on the surface has two stages. Firstly, a vibration excited molecule is absorbed by the surface with some probability

$$w_a = \nu e^{-q/T}, \quad (4)$$

where ν is a frequency of vibration of the absorbed molecule on the surface, q is the absorption heat or in our case the evaporation heat per molecule (temperature T is measured in energy units). While on the surface, the molecule removes the excitation with a probability $w_{10}^s \nu$. The probability that the molecule jumps from the surface with the velocity (3) is given by

$$W = \frac{1}{1 + w_a/w_{10}^s}. \quad (5)$$

Now we consider the evaporation of water droplets irradiated by light. Let the irradiation create and maintain a stationary non-equilibrium population of vibration excited water molecules. This is possible because water molecules possess an electric dipole moment. The concentration c^* of the vibration excited molecules is described by the following equation:

$$\frac{dc^*}{dt} = \beta I c - \frac{c^*}{\tau}, \quad (6)$$

where c is the concentration of water vapour near the droplet surface, I is the intensity of the light corresponding to the frequency of the molecular vibration ω_0 , β is a coefficient that depends on the radiation excitation cross-section of the molecular vibration, τ is a typical time

for removal of the vibration excited molecules due to the radiation transitions and to the bulk $V-T$ relaxation. Here we would like to note that the evaporation of water droplets in [3] was observed in a nitrogen atmosphere. Nitrogen molecules cannot be vibration excited by the light since they have no electric dipole moments.

A stationary concentration of the vibration excited molecules near the droplet surface is given by the relation

$$c_0^* = \tau\beta Ic. \quad (7)$$

It is known that there is a jump of the vapour concentration near the surface in a layer of width Δ (of the order of the mean free path). In this domain, there are no collisions between vapour molecules. The excited particles may leave the droplet surface with a velocity (3) exceeding the thermal velocity. Following the procedure described in [6], we may obtain the rate of evaporation of a droplet of radius R in the layer of width Δ . It may be presented in the following form:

$$J = 4\pi R^2 [(c - c^*)v_T + c^*Wv + c^*(1 - W)v_T - c_1v_T] \delta/4. \quad (8)$$

The first term in square brackets in (8) describes the flux of non-excited molecules from the droplet surface with the thermal velocity v_T ; the second term corresponds to the flux of the molecules with the velocity v (3) after de-excitation and transformation of the vibration energy; the third term is equal to the flux of the excited molecules that leave the surface with the thermal velocity; the fourth term gives the flux of molecules on the droplet surface (concentration c_1 is taken at the distance Δ from the droplet surface). The vapour condensation coefficient δ is assumed to be equal to the evaporation coefficient. A factor $1/4$ appears in (8) to account for only a quarter of the molecules moving from the surface. The evaporation rate (8) has to be equal to the rate of removal of vapour by the diffusion mechanism from the distance $R + \Delta$:

$$J = -4\pi R^2 D \frac{dc}{dr}, \quad (9)$$

where D is the diffusion coefficient of water molecules in the nitrogen atmosphere; the coordinate r is measured from the droplet surface. Due to the spherical symmetry of the problem, $\frac{dc}{dr} = -\frac{c}{r}$ and $\frac{dc}{dr}|_{r=R+\Delta} = -\frac{c}{R+\Delta}$. Inserting the last relation in (9) and expressing c_1 with the help of (8), we get

$$J = J_0 \frac{1 + W(v/v_T - 1)c^*/c}{R/(R + \Delta) + 4D/(Rv_T\delta)}, \quad (10)$$

where J_0 is the Maxwell formula for the evaporation rate. Inserting (7) in (10) and considering large droplets $R \gg \Delta$, we obtain

$$J = J_0 \frac{1 + W(v/v_T - 1)\tau\beta I}{1 + 4D/(Rv_T\delta)}. \quad (11)$$

In the domain where equation (9) holds true, bulk de-excitation of vibrations takes place as well. This results in a release of heat and in an increase in the gas temperature. Here we consider the case of a small production of excited atoms $c^*/c \ll 1$. The corresponding small increase in the temperature may weakly change the diffusion coefficient D .

Formula (11) gives the evaporation rates of droplets in different atmospheres (D is the diffusion coefficient of a droplet molecule in a particular atmosphere) provided that the radiation creates a stationary non-equilibrium vibration population of the vapour molecules. Direct excitation of the vibration degrees of freedom is possible only for molecules possessing electric dipole moments.

The employment of (11) requires knowledge of a set of phenomenological parameters. For rough estimations, we chose the typical length of the molecule-surface interaction a equal to

the amplitude of the molecular vibration. The condensation coefficient δ , to our mind, should be taken from experiment. The rest of the parameters may be found in the relevant handbooks.

Now we show that the evaporation rate of the irradiated water droplets given by (10) is in qualitative agreement with the experimental data obtained in [3]. To do this, we get rid of a phenomenological parameter, the condensation coefficient δ , by introducing a ratio of the evaporation rates of water droplets under irradiation and in the dark regime J_d (with no irradiation). The latter follows from (10) if we put the intensity of radiation $I = 0$. Further, we analyse a combination

$$J/J_d - 1 = W(v/v_T - 1)\tau\beta I. \quad (12)$$

First of all, we consider the explicit form of the probability of removing the vibration excitation $\hbar\omega_0$ and transforming it into the energy of translational motion of the molecule. Substituting (1), (4) into (5), we obtain

$$W = \frac{1}{1 + Be^{\alpha - q/T}}, \quad (13)$$

where $B = 1/[2\pi^2(2/3)^{3/2}\alpha^{1/2}]$, $\alpha = 6(\pi^2\hbar\omega_0/T)^{1/3}$. Here we set $a = [\hbar/(2m\omega_0)]^{1/2}$, where $m = M/16$ is the mass of the vibrating hydrogen atom and $v_T = (T/M)^{1/2}$. It is obvious that the temperature dependence of W is very sensitive to the factor q/T .

Let us consider the temperature range in the vicinity of $T_0 = [q^3/(216\pi^2\hbar\omega_0)]^{1/2}$ (where the index of the exponent in (13) is equal to zero). For temperatures above T_0 , the magnitude of W decreases and the difference between the evaporation rates of 'light' and 'dark' regimes diminishes. For temperatures lower than T_0 , the evaporation rate of irradiated droplets gets larger in comparison with the evaporation rate with no irradiation.

Similar situations have been observed in [3] in studies of the evaporation of water droplets in atmospheres of dry nitrogen at different pressures. At room temperature and pressures close to the normal one, there was no visible difference between the 'light' and 'dark' regimes. With decreasing pressure the evaporation rate increases (intensive evaporation) and the temperature of the water droplets is very much reduced. These droplets were even frozen. In this range of pressures, the difference between the evaporation rates was about 15%.

It would be interesting to evaluate the temperature T_0 for water droplets. A molecule of water has three infrared vibration modes with the following wavelengths: 2.73×10^{-4} cm, 6.27×10^{-4} cm, 2.66×10^{-4} cm [7]. We set the wavelength $\lambda = 3 \times 10^{-4}$ cm, which corresponds to the frequency $\omega_0 = 2\pi \times 10^{14}$ s⁻¹, and take the evaporation heat per molecule $q = 7.5 \times 10^{-13}$ erg K⁻¹. At these numerical values of the parameters, we obtain that $T_0 \approx 10^3/\pi$ lies in the region of room temperature.

The above-reported results allow us to claim that the proposed model fits the experimental results qualitatively. We believe that an appropriate choice of the parameters a and β would provide a quantitative fitting of the theory with experiment for the intensive evaporation of droplets of polar liquids (at comparatively small pressures, when the role of the bulk de-excitation may be ignored) under the action of electromagnetic radiation.

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