Diffusion of Vapor in the Presence of a Growing Droplet

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Abstract—As is shown, the solution to the diffusion equation for the concentration of vapor in the presence of a droplet growing in it, derived for the usual initial condition and equilibrium boundary conditions at the droplet surface, fails to ensure an equality between the numbers of molecules that have left the vapor due to diffusion by the current moment and those that have been included in the growing droplet. The difference between the total numbers of vapor molecules at the initial moment (when the vapor had a given uniform concentration) and at the current moment (when the size of the growing droplet is much larger than its initial size) differs from the total number of molecules in the droplet by a factor of 3/2. By substituting the usual boundary condition at the droplet surface by a time-dependent boundary condition at the surface of a constant-radius sphere with the center in the center of the growing droplet, a solution to the diffusion problem for the vapor concentration is derived. This solution describes the evolution of the vapor concentration field, which agrees with the rate of the vapor absorption by the growing droplet and with the law of the conservation of matter.

The diffusion problem is often considered in the theory of phase transitions for describing the evolution of the concentration field of a metastable phase in presence of a growing particle of the new phase [1]. For definiteness, let us consider a vapor–liquid phase transition that takes place as the excess vapor condenses on a spherical droplet. The principal aim of this paper is to construct such a solution to the diffusion problem for the vapor concentration field in the presence of a droplet growing in it that the number of droplet-constituting molecules would increase in agreement with the decrease in the number of vapor molecules in the droplet surroundings. The necessity of reaching such an agreement indeed exists, as is shown below.

Let us place the origin of the spherical coordinate system in the center of the growing droplet and denote its radius by R. Let $n(r, t)$ be the number density of vapor molecules (vapor concentration) at distance $r > R$ from the center of the growing droplet at moment t after the instantaneous creation of a vapor supersaturation with a uniform initial concentration $n(0)$ around the droplet. The radius R is assumed to be much greater than the mean free path of vapor molecules. Under this condition, the evolution of the number density $n(r, t)$ of vapor molecules in the ambient space of the growing droplet adheres to the diffusion equation

$$\frac{\partial n(r, t)}{\partial t} = \frac{D}{r}\frac{\partial^2}{\partial r^2}(rn(r, t)), \qquad (1)$$

where D is the diffusion coefficient. If we assume that a local vapor–droplet equilibrium is quickly established at the surface of the growing droplet, the boundary condition at this surface is $n(r, t)|_{r = R} = n_R$. For a vapor in equilibrium with a droplet of radius n_R, the number density R of its molecules depends on R. However, this dependence is such that the R value becomes constant (and equal to the concentration n_R of saturated vapor over a plane surface of the liquid phase) starting from very small n_∞ values. For this reason, the actually used boundary condition at the droplet surface is

$$n(r, t)|_{r = R} = n_\infty. \qquad (2)$$

Since the droplet growth is due to absorption of excess vapor molecules, the droplet radius at the current moment t changes with a rate equal to

$$\frac{d}{dt}\left(\frac{4}{3}\pi R^3\right) = 4\pi R^2 v_l D \frac{\partial n(r, t)}{\partial r}\bigg|_{r = R}, \qquad (3)$$

where v_l is the volume per molecule in the liquid phase. The v_l volume is a quantity reciprocal to the number density of molecules in the liquid phase. Differentiating the right-hand part of Eq. (3) and cancelling equal multipliers in both parts, we arrive at

$$\frac{dR}{dt} = v_l D \frac{\partial n(r, t)}{\partial r}\bigg|_{r = R}. \qquad (4)$$

The existence of a relationship between the radius of the growing droplet and the vapor concentration makes our problem nonlinear.

In applied studies, a consistent solution of the diffusion equation (1) and determination of the current size of the growing droplet according to Eq. (4) is achieved in two stages [1]. The first stage consists in determining the vapor concentration field $n(r, t)$ in the vicinity of a droplet with a fixed radius R and in calculating the diffusion flux of matter onto the droplet. The second stage

consists in determining the rate of the change in the radius R according to the diffusion flux and in finding the radius itself as a function of time t. A solution for the vapor concentration $n(r, t)$ with the fixed radius substituted by the current droplet radius $R(t)$ found at the second stage is regarded as a good approximation to the exact solution of the problem.

The possibility of solving the problem in such a succession is based on the existence of a small physical parameter

$$\alpha \equiv [2v_l(n(0) - n_\infty)]^{1/2} \qquad (5)$$

under characteristic conditions. This parameter is equal to the square root of the double density ratio of the excess vapor and condensed phase (the v_l volume is a quantity reciprocal to the number density of molecules in the liquid phase). Since the vapor density (far from the critical point) is several orders of magnitude lower than the liquid density, we have

$$\alpha \ll 1. \qquad (6)$$

For a homogeneous condensation of water vapor at $T \cong 273$ K, we obtain $\alpha \sim 5 \times 10^{-3}$. Hence, the condensation of a significant (from the diffusion standpoint) amount of vapor changes the radius of a growing droplet to a relatively small extent. Therefore, it is assumed that the solution to Eq. (1) found at $R = \mathrm{const}$ under boundary condition (2) and initial condition

$$n(r, t)|_{t=0} = n(0) \qquad (7)$$

may be used for the vapor concentration field $n(r, t)$. Such a solution has a well-known form [1]

$$n(r, t) = n(0) - [n(0) - n_\infty] \frac{R}{r} \left[1 - \Phi\left(\frac{r - R}{2\sqrt{Dt}} \right) \right], \quad (8)$$

where $\Phi\left(\dfrac{r - R}{2\sqrt{Dt}} \right)$ is the Laplacian probability integral, defined as

$$\Phi(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-\xi^2} d\xi. \qquad (9)$$

Substituting solution (8) into (4), we obtain an equation for $R(t)$:

$$\frac{dR^2}{dt} = \beta^2 \left(1 + \frac{R}{\sqrt{\pi Dt}} \right), \qquad (10)$$

where

$$\beta = [2Dv_l(n(0) - n_\infty)]^{1/2}, \qquad (11)$$

hence,

$$\beta = D^{1/2}\alpha. \qquad (12)$$

Let us assume $R(t)/(Dt)^{1/2} \ll 1$, as is confirmed below. Then Eq. (10) is reduced to $dR^2/dt = \beta^2$ and its

solution is $R^2(t) = \beta^2 t + R^2(0)$, where $R(0)$ is the droplet radius at the initial moment, when the diffusion regime of the droplet growth is activated. Let us assume $R^2(0) \sim \lambda^2$ and

$$R^2(t) \gg R^2(0), \qquad (13)$$

where λ is the mean free path of vapor molecules in the vapor–gas medium. Then at

$$R(t) \gg \lambda, \qquad (14)$$

when the droplet grows in the diffusion regime, the resultant solution $R^2(t) = \beta^2 t + R^2(0)$ is transformed into

$$R(t) = \beta t^{1/2}. \qquad (15)$$

With allowance for Eq. (12), Eq. (15) yields $R(t)/(Dt)^{1/2} = \alpha$, confirming the assumption $R(t)/(Dt)^{1/2} \ll 1$ in view of Eq. (6). Range (14) is expressed using Eqs. (15) and (12) as $t \gg \lambda^2/D\alpha^2$. At $\lambda \sim 10^{-4}$ cm, $\alpha \sim 5 \times 10^{-3}$, and $D \sim 1$ cm^2 s^{-1}, the time constraint is reduced to $t \gg 10^{-3}$ s.

Allowing for the smallness of the α parameter and thus assuming that the vapor concentration field adjusts itself to the current size of the growing droplet (in the spatial region that is representative for problems using this field) much faster than the droplet radius changes, we can write the solution for $n(r, t)$ in the form (8) with radius R from Eq. (15) substituted instead of the constant $R(t)$.

However, the concentration field $n(r, t)$ constructed using the concepts of the space and time scale hierarchy has one significant fault. To reveal it, let us calculate and compare two quantities. One of them is the difference between the total numbers of vapor molecules at the initial moment $t = 0$, when condition (7) is true, and at the current moment t, when the droplet radius $R(t)$ satisfies constraint (13). The other quantity is the total number of molecules constituting a droplet of radius $R(t)$. If inequality (13) is true, this number of molecules have virtually completely condensed in the droplet under the conditions where its radius grows with time according to Eq. (15). Let us denote the first and second quantities by $N(t)$ and $\nu(t)$, respectively. In principle, one should not expect that these quantities will be equal (as is required by the law of the conservation of matter), because the formulated solution is approximate. However, their significant difference is also unacceptable. Allowing for the initial condition (7), we obtain the $N(t)$ value as

$$N(t) = 4\pi \left(\int_R^\infty r^2 (n(0) - n(r, t)) dr \right) \Bigg|_{R=R(t)}. \qquad (16)$$

Substituting solution (8) into Eq. (16) and performing the integration, we arrive at

$$N(t) = 4\pi R(t)(n(0) - n_\infty)Dt \\ + 8\pi^{1/2} R^2(t)(n(0) - n_\infty)(Dt)^{1/2}. \qquad (17)$$

Let us use Eqs. (15) and (11) and write Eq. (17) in the form

$$N(t) = \frac{2\pi R^3(t)}{v_l} + \frac{4\pi R^3(t)}{v_l}\left(\frac{2}{\pi}\right)^{1/2}[v_l(n(0)-n_\infty)]^{1/2}. \quad (18)$$

The second term in the right-hand part of Eq. (18) should be discarded, because it has the first order of smallness with respect to the α parameter by virtue of Eq. (5). Let us write

$$N(t) \cong \frac{2\pi R^3(t)}{v_l}. \quad (19)$$

The $v(t)$ value, i.e., the number of molecules constituting a droplet of radius $R(t)$, is found as

$$v(t) = \frac{4\pi R^3(t)}{3v_l}. \quad (20)$$

Comparing Eqs. (19) and (20), we can see that

$$\frac{N(t)}{v(t)} \cong \frac{3}{2}. \quad (21)$$

Thus, if we consider the law of the conservation of matter, the use of solution (8) at the moment t and boundary surface radius $R = R(t)$ is not a good approximation to the exact solution of the problem of vapor distribution in the vicinity of a droplet growing because of vapor condensation. Meanwhile, the droplet radius growth law (15), which is determined by the local structure of the vapor concentration field near the droplet surface, is representative enough.

Note that the problem of considering the displacement of the boundary and the time dependence of the boundary concentration in solving the diffusion problem has been considered earlier, e.g., in the problem of diffusion kinetics of adsorption [2–5], where the balance of matter also plays an important role. However, those studies considered diffusion in liquid solutions, i.e., in media without small parameter (5), and model adsorption isotherms played a significant role in the closure of the equation for the boundary concentration.

Let us consider the principal aim of our communication: constructing a solution to Eq. (1) in which the evolution of the vapor concentration field would be consistent with the rate of the vapor adsorption by the droplet growing in this vapor and which would agree with the law of the conservation of matter in systems with small parameter (5).

The main element of the proposed solution is the boundary condition at the spherical surface of a given radius r_0 with the center in the center of the growing droplet. This condition is written as

$$n(r,t)|_{r=r_0} = n(0) - [n(0) - n_\infty]\frac{\beta t^{1/2}}{r_0}. \quad (22)$$

If we put $r_0 = R(t)$ in Eq. (22), it will be transformed, with allowance for Eq. (15), into boundary condition (2).

Boundary condition (22) is evidently compatible with the initial condition to the diffusion equation (1) in the form

$$n(r,t)|_{t=0} = n(0) \quad (r \geq r_0). \quad (23)$$

The main argument in favor of boundary condition (22) is that its use produces a solution to Eq. (1) that possesses properties expressed below by Eqs. (29) and (31). Meanwhile, some suggestive qualitative ideas have prompted the form of boundary condition (22). These ideas are based on the smallness of the α parameter introduced by Eq. (5) and may be briefly described as follows. The boundary surface of radius r_0 formally divides the space around the growing droplet into two regions. Boundary condition (22) refers to the diffusion equation (1) in the $r > r_0$ region. The number of vapor molecules leaving this region because of diffusion through the boundary surface of radius r_0 per unit time depends on the boundary condition maintained at this surface. In turn, the number of vapor molecules absorbed by the droplet located inside a sphere of radius r_0 per unit time depends on radius $R(t)$ of the growing droplet. To ensure an equality between the numbers of vapor molecules that have left the $r > r_0$ region because of diffusion and those that have condensed in the droplet, the boundary condition at $r = r_0$ must be related to the radius of the growing droplet. If we assume (as is justified below) that the vapor concentration field in the $R(t) < r < r_0$ region with boundary condition (2) at the surface of the growing droplet is quasi-steady-state, the condensation of vapor on the droplet must cause its radius $R(t)$ to increase according to Eq. (15) and the vapor concentration at the $r = r_0$ surface must adhere to Eq. (22). Since the quasi-steady state of the vapor concentration field actually extends beyond the $r < r_0$ region, one can expect [under condition (22)] the aforementioned equality between the number of vapor molecules leaving the $r > r_0$ region due to diffusion through the boundary surface of radius r_0 per unit time and the number of vapor molecules absorbed by the droplet located inside a sphere of radius r_0 per unit time. Thus, if we solve the diffusion equation (1) using boundary condition (22) and initial condition (23) with the fixed boundary-surface radius r_0 at the current moment substituted by the radius $R(t) = \beta t^{1/2}$ of the droplet growing due to vapor absorption, the resultant solution must display a better agreement with the law of the conservation of matter than solution (8). The assumption that the vapor concentration field in the $R(t) < r < r_0$ region is quasi-steady-state, which was used in the above reasoning, may be regarded as justified if the time (estimated as r_0^2/D) required for the establishment of a quasi-steady-state concentration field in this region is much shorter than the time required for the radius of the growing droplet to reach r_0. With allowance for Eq. (15), the latter time may be assumed to be equal to

r_0^2/β^2. Accordingly, for the required time ratio to be fulfilled, inequality $\beta^2/D \ll 1$ must be true. In view of Eq. (12), this condition is reduced to $\alpha^2 \ll 1$ and suggests the smallness of the α parameter. The above reasoning also prompts that, instead of Eq. (22), the boundary condition for Eq. (1) may be the condition of flux matching at the boundary surface with $r = r_0$. However, this approach leads to overly complicated mathematical constructions.

The general solution of Eq. (1) with the initial and boundary conditions similar to Eqs. (22) and (23), respectively, is contained, for example, in [6]. For the given actual implementation of these conditions, the solution has the form

$$n(r, t) = n(0) - \frac{2\beta t^{1/2}(n(0) - n_\infty)}{r\pi^{1/2}}$$

$$\times \int_z^\infty \left(1 - \frac{z^2}{\tau^2}\right)^{1/2} \exp(-\tau^2)d\tau, \tag{24}$$

where

$$z = \frac{r - r_0}{2(Dt)^{1/2}}. \tag{25}$$

The right-hand part of condition (22) at a fixed r_0 is time-dependent, whereas the right-hand part of condition (2) at a fixed R is not. This is the reason for the difference between solutions (24) and (8). This difference makes it possible to establish that solution (24) with $r_0 = R(t)$ in the notation of Eq. (25) agrees with the law of the conservation of matter.

Solution (24) has two important properties. To formulate the first of them, let us calculate the number $j(t)$ of vapor molecules carried inside the boundary surface of radius $r_0 = R(t)$ by the diffusion flux per unit time, using Eq. (15) for $R(t)$. By definition, we have

$$j(t) = 4\pi r^2 D \frac{\partial n(r, t)}{\partial r}\bigg|_{r = R(t)}. \tag{26}$$

Using solution (24) in Eq. (26), assuming $r_0 = R(t)$ in it, and performing the necessary calculations, we arrive at

$$j(t) = 4\pi\beta t^{1/2}D(n(0) - n_\infty)[1 + R(t)/(Dt)^{1/2}], \tag{27}$$

with allowance made for

$$\lim_{z \to 0} \frac{2}{\pi^{1/2}}z\int_z^\infty \frac{\exp(-\tau^2)}{\tau(\tau^2 - z^2)^{1/2}}d\tau = \pi^{1/2}. \tag{28}$$

In accordance with Eqs. (15), (12), and (6), we obtain $R(t)/(Dt)^{1/2} = \alpha \ll 1$. Then Eq. (27) yields

$$j(t) \cong 4\pi\beta t^{1/2}D(n(0) - n_\infty). \tag{29}$$

In view of Eqs. (11), (15), and (20), equality (29) implies that the number of vapor molecules (in the principal order by the small parameter α) carried by the dif-

fusion flux per unit time inside a sphere with the droplet radius $R(t)$, which depends on t according to Eq. (15), is equal to the number of molecules that must be attached to the droplet inside the sphere per unit time so that Eq. (15) would be true. This statement, which is based on the proposed solution (24), thus agrees with the result obtained on the basis of solution (8). The second property of solution (24) declared in this paragraph will show its serious advantage compared to solution (8).

Let us calculate the $N(t)$ value defined by Eq. (16) using solution (24) with $r_0 = R(t)$ in that equation. We obtain

$$N(t) = 16\pi^{1/2}\beta t D^{1/2}(n(0) - n_\infty)$$

$$\times \int_0^\infty [2(Dt)^{1/2}z + R(t)]dz\int_z^\infty \left(1 - \frac{z^2}{\tau^2}\right)^{1/2} \exp(-\tau^2)d\tau, \tag{30}$$

with allowance made for notation (25), where $r_0 = R(t)$. Let us consider Eqs. (15) and (12) and the numerical values of the integrals

$$\frac{2}{\pi^{1/2}}\int_0^\infty z dz\int_z^\infty \left(1 - \frac{z^2}{\tau^2}\right)^{1/2} \exp(-\tau^2)d\tau = \frac{1}{6},$$

$$\frac{2}{\pi^{1/2}}\int_0^\infty dz\int_z^\infty \left(1 - \frac{z^2}{\tau^2}\right)^{1/2} \exp(-\tau^2)d\tau \cong 0.44.$$

We arrive at

$$N(t) = \frac{4\pi R^3(t)}{3v_l}(1 + 1.31\alpha). \tag{31}$$

Comparing Eqs. (31) and (20), we see that, in the principal order by the small parameter α, the difference $N(t)$ between the total numbers of vapor molecules at the initial moment $t = 0$, when Eq. (23) is true, and at the current moment t, when the droplet radius $R(t)$ satisfies constraint (13), turns out to be equal to the total number $v(t)$ of molecules in a droplet of radius $R(t)$.

Thus, solution (24), in contrast to solution (8), shows a virtually exact agreement with the law of the conservation of matter. This property of solution (24) is not only important in principle but may also have a great significance for some problems of the nucleation theory [7] and adsorption from the gaseous phase, where the vapor concentration field in the presence of a growing droplet should be described with a sufficiently high accuracy.

The quantitative difference between the vapor concentration fields in the presence of a growing droplet constructed using solutions (8) and (24) depends on the α parameter value. To estimate this difference, it is convenient to consider the relative decrease $\varphi(r, t)$ in the vapor supersaturation, defined as
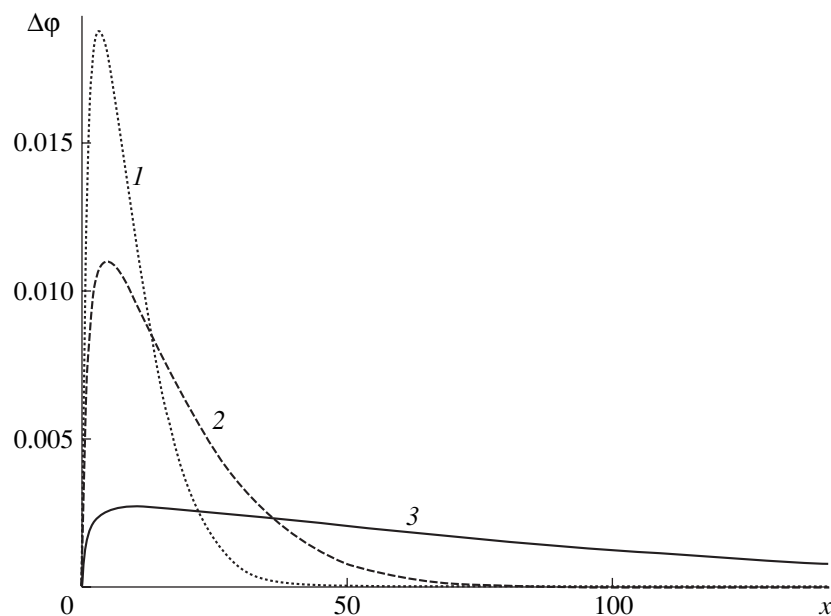
The difference $\Delta\varphi$ between the values $\varphi(r, t)$ of the relative decrease in the vapor supersaturation found using solutions (8) and (24), respectively. Curves *1–3* correspond to $\alpha = 0.1$, 0.05, and 0.01, respectively. *x* denotes the $r/R(t)$ ratio.

$$\varphi(r, t) = \frac{n(0) - n(r, t)}{n(0) - n_\infty}. \qquad (32)$$

If the *r* distance is measured in units of the current radius $R(t) = \beta t^{1/2}$ of the growing droplet, it is easily seen that the relative decrease $\varphi(r, t)$ in the vapor supersaturation does not directly depend on time, no matter whether it is determined using solution (8) or (24). The plots in the figure show the difference $\Delta\varphi$ between the values of the $\varphi(r, t)$ function found using solutions (8) and (24), respectively. Curves *1*, *2*, and *3* correspond to $\alpha = 0.1$, 0.05, and 0.01, respectively. The curves demonstrate a minor discrepancy between the two solutions, and the imbalance [expressed by Eq. (21) based on solution (8)] between the substance carried from the vapor actually by diffusion and the substance that has formed the droplet grown in the vapor is accumulated as a result of integration over the vapor volume.

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