JOURNAL OF CHEMICAL PHYSICS VOLUME 121, NUMBER 1 1 JULY 2004

Study of nonsteady diffusional growth of a droplet in a supersaturated vapor: Treatment of the moving boundary and material balance

A. P. Grinin, A. K. Shchekin, F. M. Kuni, and E. A. Grinina
Department of Theoretical Physics, Physics Research Institute, St Petersburg State University,
1 Ulyanovskaya Street, Petrodvorets, St-Petersburg 198504, Russia

H. Reiss[a]
Department of Chemistry and Biochemistry, UCLA, Los Angeles, California 90095

(Received 15 January 2004; accepted 22 March 2004)

A new mathematical treatment of the problem of droplet growth via diffusion of molecules from a supersaturated vapor is presented. The theory is based on a semiquantitative analysis with good physical arguments and is justified by its reasonable predictions. For example it recovers the time honored growth law in which, to a high degree of approximation, the droplet radius increases with the square root of time. Also, to a high degree of approximation, it preserves material balance such that, at any time, the number of molecules lost from the vapor equals the number in the droplet. Estimates of the remaining approximational error are provided. On another issue, we show that, in contrast, the conventional treatment of droplet growth does not maintain material balance. This issue could be especially important for the nucleation of another droplet in the vicinity of the growing droplet where the rate of nucleation depends exponentially on supersaturation. Suggestions for further improvement of rigor are discussed. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1740752]

I. NATURE OF THE PROBLEM

Diffusion controlled growth of a droplet in a supersaturated vapor has been considered repeatedly in the literature.[1–6] The phenomenon is of major importance to colloid chemistry, atmospheric science, and many other disciplines, including the new endeavor of nanotechnology. However, even after many years, an exact analytical solution of the associated boundary value problem is not available, although relatively satisfactory approximate solutions were achieved at an early stage of inquiry. The chief impediment to an exact solution has been the movement of the boundary (surface of the droplet) during droplet growth, resulting in a decidedly nonlinear situation.

Favored paths to approximation have usually incorporated the following steps:

1. In the simplest approach, the differential equation describing the diffusional transport of molecules to the droplet, based on the continuity equation, into which Fick's law has been substituted, is first relaxed by setting the time derivative equal to zero. This destroys the pointwise conservation of molecules except for the case of steady state transport. In the case of spherical symmetry with which we are concerned, the solution of the remaining differential equation (now an ordinary differential equation) is simply

$$n(r)=A+\frac{B}{r}, \tag{1}$$

where r is the radial coordinate of position with origin at the center of the droplet, n is the concentration of diffusing molecules, and A and B are constants which can be determined by the application of time independent boundary conditions, one of which is applied at the droplet surface, assumed stationary and located at $r=R$. It is clear that this solution is inappropriate for a nonfixed or moving boundary.

2. Nevertheless, a more or less *ad hoc* partial solution to the problem has usually been achieved by accommodating time-dependent boundary conditions (e.g., movement of the boundary) by allowing A and B to depend on time and to be determined by these conditions. The result is a concentration profile that varies with time and which may be characterized as "quasisteady." Then the diffusion flux into the droplet is evaluated using the time dependent gradient obtained from this profile and, from it, the rate of growth of the droplet is established. The qualitative rationale behind this procedure is that (at least in a vapor) the rate of change of the radius of a dense droplet is small compared to a typical distance through which a molecule diffuses in unit time. Indeed, it is not a bad approximation and it leads to the well-known growth law

$$R(t)=\beta t^{1/2}, \tag{2}$$

where t is time and β is a constant, and it has been assumed that $R(0)=0$.

A primary difficulty with the above approximation is its failure to maintain material balance. This is to be expected since Eq. (1) is the long time limit of the following expression.

$$n(r,t)=n_0-(n_0-n_\infty)\frac{R}{r}\left[1-\Phi\left(\frac{r-R}{2\sqrt{Dt}}\right)\right], \qquad r\geqslant R, \tag{3}$$

---

[a] Author to whom correspondence should be addressed. Electronic mail: reiss@chem.ucla.edu

where $n(r,t)$ is the *nonsteady* concentration of diffusant at r at time t, and where R is a "fixed" radius of a sink (droplet) on whose surface the concentration of diffusant is maintained constant at n_∞ the equilibrium vapor density of the drop, while $n_0 = n(r,0) > n_\infty$ is the initial concentration of vapor molecules in the diffusion field extending between $r=R$ and $r=\infty$. Finally, D is the diffusivity of a vapor molecule, while

$$\Phi(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-\xi^2} d\xi, \tag{4}$$

is the Laplacian probability integral or error function.

Equation (3) is a solution of the continuity equation,

$$\frac{\partial n(r,t)}{\partial t} = \frac{D}{r} \frac{\partial^2}{\partial r^2}(rn(r,t)), \tag{5}$$

into which Fick's law has been substituted, and which is subject to the following initial and boundary conditions

$$n(r,0) = n_0, \quad r > R, \tag{6}$$

$$n(R,t) = n_\infty. \tag{7}$$

Since Eq. (3) satisfies the continuity equation, it obviously maintains material balance in the sense that the integrated flux, i.e., the flux of molecules entering the sphere of radius R integrated over the time t, is equal to the decrease of the number of vapor molecules in the diffusion field over the same time. However, it is essential to note that the equation accomplishes this using a *nonsteady* $n(r,t)$ and a *stationary* boundary at $r=R$ where the concentration of molecules does not vary with time. Furthermore, at infinite time, Eq. (3) converges on a true steady state in which the time derivative in Eq. (5) converges on zero. However, it is clear, even without a quantitative analysis, that as soon as the boundary at R is allowed to move, there can *never* be a true steady state. In the conventional approach leading to Eq. (2) and Eq. (5) with the time derivative suppressed, is used in conjunction with the boundary condition, Eq. (7), applied at a *moving* boundary $R(t)$. Clearly, this involves an immediate contradiction since, with a moving boundary the diffusion cannot be steady so that $\partial n/\partial t$ cannot vanish. Thus, it is evident on an *a priori* basis that the conventional approach cannot maintain material balance. By how much it fails is a matter for quantitative study, some of which we address below. We remark that even a modest failure could represent a significant problem for an associated theory of nucleation in the surrounding vapor, since nucleation rates depend so sensitively on supersaturation. On the other hand, for the rate of droplet growth, a modest failure would not be so serious, since the growth rate is more or less linear in the diffusant gradient outside of the droplet.

The question then arises as to how to improve the approximation inherent in the conventional approach so that material balance is at least closely, even if not exactly, achieved. In the pursuit of this goal we can steal a hint from Eq. (3) which does not represent a steady state and achieves material balance, among other things, by referring to a *fixed* boundary at $r=R$. Can we somehow involve some fixed boundary in the moving boundary theory and, even though diffusion might not be steady, maintain material balance?

In the following sections we develop such an approach in which both a fixed boundary and a nonsteady $n(r,t)$ play roles, and where Eq. (2) is eventually generated even though material balance is *almost* achieved. First, however, we return to the conventional approach in order to both demonstrate the magnitude of the failure of material balance and to introduce some important parameters.

II. QUANTITATIVE CRITIQUE OF THE CONVENTIONAL APPROACH AND THE FAILURE OF MATERIAL BALANCE

The question of the spatial distribution of the vapor in the vicinity of a growing droplet has been considered in a nonspecific way by Goodrich.[4] He converted the diffusional boundary value problem containing an outward-moving droplet boundary into two coupled integral equations. However, he focused on the time dependence of the droplet radius and on an iterative solution leading to the equation describing that time dependence. Equation (2) was confirmed as the zeroth-order term of an expansion in powers of the square root of the ratio of excess vapor density to liquid density, and corrections to Eq. (2) were found as higher order terms in the expansion. However, the behavior of the vapor density outside of the droplet was not studied.

Returning to the conventional approach, since the change of volume of the droplet is due to the diffusion flux of molecules coming from the vapor, the time rate of change of R is given by

$$\frac{dR}{dt} = v_l D \left. \frac{\partial n(r,t)}{\partial r} \right|_{r=R}, \tag{8}$$

where v_l is the volume per molecule in the liquid. This relationship between the radius of the growing droplet and the vapor concentration renders the problem nonlinear. Approximating the diffusion as quasistationary so that Eq. (1), with A and B regarded as functions of time, applies, and using the boundary condition, Eq. (7), together with a second boundary condition, namely

$$n(\infty,t) = n_0, \tag{9}$$

yields

$$n(r,t) = n_0 - \frac{(n_0 - n_\infty)R(t)}{r}. \tag{10}$$

Substitution of this result into Eq. (8) yields, after integration with respect to time, Eq. (2) with

$$\beta \equiv [2Dv_l(n_0 - n_\infty)]^{1/2}. \tag{11}$$

It is instructive to examine a revised version of Eq. (3) obtained by substituting $R(t)$ of Eq. (2) [with β given by Eq. (11)], in place of R. Clearly, since R is then no longer constant, Eq. (3) is no longer an exact solution of the boundary value problem that led to Eq. (3) in the first place. However, we can show that under the physical conditions of droplet growth in the vapor, the revised Eq. (3) can be used to derive an equation only slightly different from Eq. (2). To show this we proceed as follows. Substitute the revised Eq. (3) into Eq. (8) to obtain

$$\frac{dR^2}{dt}=\beta^2\left(1+\frac{R(t)}{\sqrt{\pi Dt}}\right)=\beta^2\left(1+\frac{2\alpha}{\sqrt{\pi}}\right), \tag{12}$$

where

$$\beta=2D^{1/2}\alpha, \tag{13}$$

and α is the dimensionless parameter

$$\alpha\equiv[v_l(n_0-n_\infty)/2]^{1/2}. \tag{14}$$

The usefulness of α will lie in the fact that it is very small in the sense that $\alpha\ll 1$. It is actually equal to the square root of one half of the ratio of n_0-n_∞, the excess vapor density, to $1/v_l$ the density of the liquid droplet. Hence, the condensation of a significant amount of vapor changes the radius of a growing droplet only relatively slightly. For example, for the condensation of water vapor at $T\cong 273\,\mathrm{K}$, we obtain $\alpha\sim 5\cdot 10^{-3}$. We return later to the effects of this small parameter.

Assume $R(t)/(Dt)^{1/2}\ll 1$. This amounts to assuming that the radius of the droplet at any time t is much smaller than the distance through which a molecule in the vapor can diffuse during the same time, and is an idea obviously suggested by the fact that the liquid is so dense compared to the vapor. A more quantitative confirmation of this fact is presented below. If this is the case, Eq. (12) 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 time zero, i.e., when diffusional growth of the droplet is activated, i.e., the time at which $R^2(0)\approx\lambda^2$ where λ is the mean free path of molecules in the vapor. Then it does follow that:

$$R^2(t)\gg R^2(0)\approx\lambda^2, \tag{15}$$

so that $R^2(t)=\beta^2 t+R^2(0)$ may be well approximated by

$$R(t)=\beta t^{1/2}=2D^{1/2}\alpha t^{1/2}, \tag{16}$$

which is identical to Eq. (2).

According to Eq. (16) we may write $R(t)/(Dt)^{1/2}=2\alpha$, confirming the assumption $R(t)/(Dt)^{1/2}\ll 1$, since α has been shown to be so much less than unity [in view of Eq. (14)]. The time regime, within which Eq. (15) is valid, is bounded from below. Using Eq. (16) in Eq. (15), we find

$$R^2=\beta^2 t=4D\alpha^2 t\gg\lambda^2 \quad\text{or}\quad t\gg\frac{\lambda^2}{4D\alpha^2}=t_{\text{lower-bound}}. \tag{17}$$

With $\lambda\sim 10^{-4}\,\mathrm{cm}$, $\alpha\sim 5\cdot 10^{-3}$, and $D\sim 1\,\mathrm{cm^2\,s^{-1}}$, the lower bound $t_{\text{lower-bound}}$, for the time beyond which Eq. (15) is valid, is therefore $10^{-3}\,\mathrm{s}$. This means that the quasisteady state is established very rapidly in comparison to the time required for the droplet to grow, and gives support to the quasisteady approximation.

The reader should note that we used the smallness of α in neglecting the second term in parentheses in Eq. (12) and the smallness of $R(0)$ in arguing for the neglect of the initial size of the droplet so as to reproduce Eq. (2), in connection with which it had been assumed that $R(0)=0$. What we have shown is that, starting with the solution of a boundary value problem in which R was fixed and where material balance was maintained, the fixed R could be replaced by an R varying with time in accordance with Eq. (2), i.e., by an $R(t)$ obtained through the use of the quasisteady approximation, and that, to a very high degree of approximation, this step returned the quasisteady $R(t)$. Along the way it was demonstrated that this good result owed its validity to the fact that the density of the liquid was so much greater than that of the vapor and to the fact that the distance through which a molecule diffused during time t was always much larger than the droplet radius.

What has not been shown is that the result, besides furnishing a good approximation to the time dependence of the droplet radius, also provides a good approximation to material balance. In fact, as we now show, it fails in this respect.

At any time t the number of molecules that have been extracted (as a result of droplet growth) from the vapor must be given by

$$N(t)=\tfrac{4}{3}\pi[R(t)]^3 n_0+4\pi\left(\int_{R(t)}^{\infty}r^2(n_0-n(r,t))dr\right). \tag{18}$$

In this equation, the first term on the right is the number of molecules that have disappeared from the vapor in the region occupied by the droplet because there is no longer any vapor in that region. The second term is clearly the number of molecules that have disappeared from the vapor in the region outside of the droplet. Substitution of Eq. (16) into the first term on the right side of Eq. (18) shows that this term is of the order of α^3 and, since α is such a small quantity, the first term may be discarded. Substitution of the revised Eq. (3) into the second term on the right side of Eq. (18), and performance of the integration, yields (after discarding the first term)

$$N(t)=4\pi R(t)(n_0-n_\infty)Dt+8\pi^{1/2}R^2(t)(n_0-n_\infty)(Dt)^{1/2}. \tag{19}$$

Equations (2) and (11) may be used to write Eq. (19) in the form

$$N(t)=\frac{2\pi R^3(t)}{v_l}+\frac{4\pi R^3(t)}{v_l}\left(\frac{2}{\pi}\right)^{1/2}[v_l(n_0-n_\infty)]^{1/2}. \tag{20}$$

The second term on the right of this equation may be discarded since it is of the first order in the small parameter α. Thus we can write

$$N(t)\approx\frac{2\pi[R(t)]^3}{v_l}. \tag{21}$$

Now the number of molecules in the droplet at time t is

$$\nu(t)=\frac{4\pi[R(t)]^3}{3v_l}. \tag{22}$$

From Eqs. (19) and (20) we find

$$\frac{N(t)}{\nu(t)}\approx\frac{3}{2}. \tag{23}$$

Thus, it is obvious that the conventional quasisteady approach to the solution of the moving boundary problem does not maintain material balance between the vapor and the droplet, even though, as we have shown, it leads to a viable approximation for the time rate of change of the droplet radius. Although the failure of this ratio to maintain material balance is only of the order of 50% it could still be significant as far as nucleation in the vapor surrounding the droplet is concerned.

In closing this section, it should be noted that other attempts have been made to ameliorate the material balance problem. These include the use of the "method of finite zone continuity"[6] as well as approaches used in studies of diffusional kinetics in adsorption.[7–10] However, these approaches are not detailed enough to be used in a theory of nucleation in a nonuniform medium.

III. REFORMULATION: MAINTENANCE OF BOTH MATERIAL BALANCE AND CONVENTIONAL GROWTH RATE

Over the years, the conventional theoretical growth rate, $R(t)=\beta t^{1/2}$, has been shown to agree quite closely with experiment, even though, as demonstrated in the previous section, the associated theory does not predict strict material balance. A desirable goal would, therefore, be the development of a theory that predicts the conventional rate as well as material balance, even if only to a high degree of approximation. The ease of formulation of such a theory can benefit appreciably from the physical insight gained in the last section from the consideration of the quasisteady state.

At the outset, it should be indicated that we will not follow absolutely rigorous paths. This was the case in the evolution of the conventional theory where physical insight played an important role and where the justification of the theory was partly connected to its success in predicting the results of experiment. A similar mixture of insight and mathematical rigor are involved in the construction of the refined theory that maintains material balance as well as the conventional growth law for the droplet.

It is convenient to begin with the infinite time limit of Eq. (3). Because $\Phi(0)=0$, with R finite and $t\to\infty$, this limiting form is

$$n(r,t)=n_0-\frac{(n_0-n_\infty)}{r}R\to n_0-\frac{(n_0-n_\infty)}{r}R(t),$$
$$R\to R(t)=\beta t^{1/2}, \tag{24}$$

where the second expression is simply the limiting form of the revised Eq. (3) with $R(t)$ substituted for R. However, we also note that the second form is identical with Eq. (10) which was derived from Eq. (1) using Eqs. (7)–(9). But these equations are the foundation of the conventional quasisteady state approach so that the limiting form of the revised Eq. (3) corresponds to the conventional theory.

Now, as Eq. (17) indicates the quasisteady state is established very rapidly. This is especially true at small values of r [λ in Eq. (17) is simply an example of a small value of r]. Thus for a finite range of r in the neighborhood of the droplet surface, say out to $r=R^*$ we may assume that the quasisteady state prevails. We can thus choose a fixed value of R, say $r=R_0$, such that $R_0<R^*$, and Eq. (24) will require that

$$n(R_0,t)=n_0-[n_0-n_\infty]\frac{\beta t^{1/2}}{R_0}. \tag{25}$$

Now, in spite of the quasisteady approximation, the actual physical process is governed by the nonsteady continuity equation, namely Eq. (5). The real process is, therefore, everywhere nonsteady. It is, therefore, nonsteady at $r>R_0$. We can try to characterize this nonsteady behavior in the domain, $r>R_0$, by solving Eq. (5) subject to a boundary condition at $r=R_0$ that is algebraically identical to Eq. (25), i.e.,

$$n(r,t)=n_0-[n_0-n_\infty]\frac{\beta t^{1/2}}{R_0},\quad r=R_0, \tag{26}$$

together with the initial condition

$$n(r,0)=n_0,\quad r\geqslant R_0, \tag{27}$$

with which Eq. (26) is consistent. The solution of this boundary value problem is[11]

$$n(r,t)=n_0-\frac{2\beta t^{1/2}(n_0-n_\infty)}{\pi^{1/2}r}\int_z^\infty\left(1-\frac{z^2}{\tau^2}\right)^{1/2}\exp(-\tau^2)d\tau,$$
$$r\geqslant R_0, \tag{28}$$

where

$$z=\frac{r-R_0}{2(Dt)^{1/2}}. \tag{29}$$

Equation (28) will form the basis of our new approximation. Besides being an exact solution, it satisfies the continuity equation and a boundary condition, Eq. (26), at a *fixed* boundary. Therefore, it conserves material, i.e., the flux of molecules at $r=R_0$, integrated over time equals, at time *t*, $\int_{R_0}^\infty[n_0-n(r,t)]4\pi r^2dr$.

In the region $r<R_0$ where Eq. (28) does *not* provide an exact description of the transport process, Eq. (24) has been assumed to provide a good approximate description of transport. Indeed, as an approximation, we have assumed that Eq. (24) continues to provide a good description out to $r=R^*>R_0$. This implies that Eqs. (24) and (28) overlap, not exactly, but rather well in the region, $R_0\leqslant r\leqslant R^*$. Furthermore, we *know* that the two solutions yield *exactly* the same value of $n(r,t)$ at $r=R_0$. This follows from the identity of Eqs. (25) and (26). Thus, as far as the vapor density is concerned, the two solutions are matched at the boundary, $r=R_0$ between the respective regions in which they apply.

At $r=R_0$, it would also be desirable to match their derivatives with respect to r. Then, the flux leaving the vapor beyond $r=R_0$, would equal the flux in the region $r<R_0$, and since the latter flux is quasisteady almost all of the molecules leaving the former region and entering the latter region would reach the sink represented by the surface of the droplet. Indeed, if the flux was *steady* rather than only quasisteady, all of the molecules would reach the droplet and be absorbed. However, the flux in question, besides being only quasisteady, is not exactly matched to the flux leaving the region $r>R_0$. These two features contribute to the "approximate" nature of the theory. At the same time, because "quasisteady" is almost "steady," and because of the above mentioned probable good overlap between the solutions in the region $R_0 \leqslant r \leqslant R^*$, the approximation should be good. As indicated earlier, ultimately, its validity will depend upon how well the theory agrees with experiment.

The number of molecules lost in traversing the region $r < R_0$ can be minimized by choosing R_0 as close to $R(t)$ as possible, i.e., by making the region $r < R_0$ as small as possible. Actually, we can take the *ad hoc* step of setting $R_0 = R(t) = \beta t^{1/2}$. This, of course, while eliminating the region $r < R_0$, will partially invalidate the solution, Eq. (28), which is predicated on R_0 representing a *fixed* boundary, but it is similar to the step taken in the conventional quasisteady approach which provides a pretty good prediction of the rate of droplet growth. Again, the adequacy of the approximation will depend upon the goodness of the prediction that it allows. Notice that, if we do take this step, the boundary condition, Eq. (26), will be reduced to $n(R,t) = n_\infty$ which is identical with Eq. (7) and is, therefore, exactly the boundary condition that we want!

A brief overview of the new approximation is in order. First we note that Eq. (28) not only establishes material balance, but it also describes a nonsteady situation such that the time derivative in the continuity equation is not set to zero. This represents a considerable departure from the conventional approach where the time derivative is actually set to zero in order to generate an equation like Eq. (1). Then by setting R_0 equal to $R(t)$, the approximation eliminates the quasisteady region that dominates the conventional approach. Of course, this approximation destroys the rigor of Eq. (26), but it preserves the acceptable droplet growth law, Eq. (2). On the other hand it might go much further than the conventional approach in maintaining material balance. Whether or not it does is examined in the following section.

It is also possible to give a semiquantitative argument as to why the replacement of the fixed boundary R_0 with the moving one $R(t)$ does not seriously damage the original mathematical result. The argument proceeds as follows. At time *t*, the sphere of fixed radius R_0 may, during a following time interval Δt, be regarded as the future radius $R(t+\Delta t)$ of the droplet at the time $t+\Delta t$. This means that the fixed R_0, during Δt, must be only slightly larger than $R(t)$. During the interval Δt, the flux through the sphere of radius R_0 can be evaluated from the exact result, Eq. (28), that contains the parameter R_0. Since, during Δt, the volume $(4\pi/3)[R_0^3 - [R(t)]]^3$ is so small, very few molecules could accumulate in it. Furthermore, this flux quickly achieves a quasisteady state. Thus, essentially all of the molecules diffusing through the outer sphere of radius R_0 are absorbed by the droplet. During the next interval of time, the same procedure can be used. Thus, throughout the growth of the droplet only a small error will be generated by regarding R_0 as $R(t)$.

The assumption that the concentration profile is quasisteady in the region where *r* satisfies the inequality $R(t) < r < R_0$ may be justified if the time (estimated as R_0^2/D) required for the establishment of a quasisteady profile in this region is much shorter than the time required for the radius of the growing droplet to reach R_0. Using Eq. (2), the latter time may be estimated as R_0^2/β^2. Thus, for the required time ratio to be fulfilled, the inequality $\beta^2/D \ll 1$ must be true. In view of Eq. (13), this condition is reduced to $\alpha^2 \ll 1$ which has been shown to be true.

In the procedure just described, the zero of time in each time step Δt is essentially the actual time at the beginning of that step, and the initial size of the droplet is the actual size at the beginning of Δt. Beyond R_0 the transport is governed by the differential equation that satisfies the time-dependent boundary condition at R_0.

One might ask why the situation is not reduced to the conventional approach when R_0 is replaced by $R(t)$, since, in that approach, the fixed boundary at R in Eq. (3) is also replaced by $R(t)$. The answer is that, in the conventional approach, the condition, Eq. (7), at the fixed boundary is independent of time and, therefore, cannot match a quasisteady concentration, like that given by Eq. (25), at a position $r = R$ slightly beyond $R(t)$. In contrast, in the new approach, the new time-dependent condition at R_0, Eq. (26), can match the quasisteady concentration and, therefore, assures the continuity of the concentration profile at the R_0 interface between the quasisteady solution and the nonsteady solution given by Eq. (28). Then when the quasisteady region is essentially eliminated by the replacement of R_0 by $R(t)$, transport in the diffusion field will be nonsteady and to a high degree of approximation will satisfy the continuity equation with a nonzero derivative, so that material balance will be maintained to the same degree of approximation. Thus the new approach should *almost* establish material balance while, at the same time preserving Eq. (2). How well it succeeds in this respect is the subject of the following section.

IV. CONVENTIONAL GROWTH LAW AND MATERIAL BALANCE IN THE NEW APPROACH

In connection with the conventional approach, it was demonstrated that the conventional rate law, Eq. (16), was consistent (within an error of order α) with Eq. (12) which was derivable from Eq. (3) with $R(t)$ substituted for the equation's fixed *R*, i.e., from the revised Eq. (3). In effect, the law was derived from the revised equation. We will now show that the same rate law can be derived from Eq. (28) with the conventional $R(t)$ substituted for the fixed R_0, i.e., derived from a revised Eq. (28).

The conventional growth law, Eq. (16), can be written as

$$\frac{1}{\upsilon_l}\frac{d}{dt}\left(\frac{4\pi[R(t)]^3}{3}\right) = 4\pi R(t) D(n_0 - n_\infty)$$

$$= 4\pi\beta t^{1/2} D(n_0 - n_\infty) = j(t), \tag{30}$$

where $j(t)$ is the number of molecules passing into the spherical volume of radius $R(t)$ per unit time. That this is just another form of Eq. (16) can easily be shown by integrating the differential equation on the left, subject to $R(0) = 0$.

Now it is clear that $j(t)$ can also be written as

$$j(t) = 4\pi r^2 D \left.\frac{\partial n(r,t)}{\partial r}\right|_{r=R(t)}, \tag{31}$$

since the right-hand side of this equation represents the total diffusive flux through the spherical surface of radius $R(t)$.

Since we now wish to examine the properties of the new approach, $n(r,t)$ given by the revised Eq. (28) will now be substituted into Eq. (31) to obtain

$$j(t)=4\pi\beta t^{1/2}D(n_0-n_\infty)[1+R(t)/(Dt)^{1/2}]. \tag{32}$$

In the algebraic manipulations leading to Eq. (32) the following relation must be used

$$\lim_{z\to 0}\frac{2}{\pi^{1/2}}z\int_z^\infty\frac{\exp(-\tau^2)}{\tau(\tau^2-z^2)^{1/2}}d\tau=\pi^{1/2}, \tag{33}$$

where z is given by Eq. (29). From Eq. (16), we find $R(t)/(Dt)^{1/2}=2\alpha\ll 1$. Thus, with a small error of order α, this ratio can be neglected in Eq. (32), yielding the result

$$j(t)\cong 4\pi\beta t^{1/2}D(n_0-n_\infty). \tag{34}$$

This relation is identical to the right-hand equation in Eq. (32), and shows that the revised Eq. (28) is consistent, to within a small error of order α, with the conventional growth law and that, in effect, the growth law can be derived from the revised Eq. (28). Thus the new approach preserves the conventional growth law.

Next, we examine how closely the new (nonsteady) approach leads to material balance. For this purpose $N(t)$, defined in connection with Eq. (18), must be evaluated using $n(r,t)$ prescribed by the revised Eq. (28). The result is

$$N(t)=16\pi^{1/2}\beta t D^{1/2}(n_0-n_\infty)\int_0^\infty[2(Dt)^{1/2}z+R(t)]dz \times\int_z^\infty\left(1-\frac{z^2}{\tau^2}\right)^{1/2}\exp(-\tau^2)d\tau, \tag{35}$$

where z is given by Eq. (29). Using Eq. (16), and the following definite integrals:

$$\frac{2}{\pi^{1/2}}\int_0^\infty z\,dz\int_z^\infty\left(1-\frac{z^2}{\tau^2}\right)^{1/2}\exp(-\tau^2)d\tau=\frac{1}{6},$$
$$\frac{2}{\pi^{1/2}}\int_0^\infty dz\int_z^\infty\left(1-\frac{z^2}{\tau^2}\right)^{1/2}\exp(-\tau^2)d\tau\cong 0.44, \tag{36}$$

in Eq. (35), we obtain

$$N(t)=\frac{4\pi R^3(t)}{3v_l}(1+2.62\alpha). \tag{37}$$

Comparing Eq. (37) with Eq. (22), shows that, to within a small error of order α, $N(t)$ the number of molecules lost from the vapor equals the number of molecules accumulated in the drop. Thus the new approach maintains material balance to within a very small error of order α.

V. USE OF THE α-TERM AS A CORRECTION AND CONCLUDING REMARKS

The analysis of the preceding sections has shown that the new approach, related to the revised Eq. (28), preserves both material balance and the conventional droplet growth law, Eq. (2), to within errors of order α. In contrast, the conventional approach related to the revised Eq. (3), generates a much larger error [see Eq. (23)] in regard to material balance. One might argue that the ratio 3/2 in Eq. (23) is still only slightly different from the unity that would represent material balance, so that the conventional approach still provides an acceptable approximation. This is true for some purposes, for example, as far as the droplet growth law is concerned, but its accuracy is questionable in regard to phenomena (in the neighborhood of a growing droplet) such as nucleation[12] and adsorption from the gaseous phase, where rates can be extremely sensitive to the concentration profile in the vapor.

The parameter α, defined by Eq. (14), is essentially a measure of the ratio of the vapor density to that of the liquid. Its smallness emphasizes the fact that, during growth, the droplet radius changes very slowly in comparison to the rate of molecular transport in the vapor, so that to a first approximation, the droplet surface might be regarded as stationary. Even before any quantitative analysis, this supports a qualitative explanation as to why both the conventional and the new approaches lead to a satisfactory droplet growth law. This raises the question of whether the exact solution to the problem can be represented as an expansion in powers of α. If this were the case, then in Eq. (32), retaining the terms of order α might result in even more accurate approximations. However, for this to be the case, the terms of order α in, for example, Eq. (32) for $j(t)$ and in a corresponding equation for $d\nu(t)/dt$, the rate of change of the number of molecules in the droplet, would have to be linear terms in bona fide α expansions. There is really no assurance that this is the case. In fact, expressions for $d\nu/dt$ obtained from the new approach, based on Eq. (28), and from the approach of Goodrich,[4] yield different expressions for the α-terms. Only one of these expressions could be right and it is obviously likely that both are wrong.

For the record, the two expressions are presented as Eqs. (38) and (39), below. The formula from the new approach follows from Eqs. (4), (31), and (32), and is

$$\frac{d\nu}{dt}=4\pi\beta t^{1/2}D(n_0-n_\infty)\left[1+\frac{R(t)}{(Dt)^{1/2}}\right]. \tag{38}$$

The formula obtained by Goodrich [Eq. (13) in Ref. 4], expressed in our notation, is

$$\frac{d\nu_G}{dt}=4\pi R(t)D(n_0-n_\infty) \times\left[1+\frac{1}{(4\pi D)^{1/2}}\int_0^t\frac{dR(\tau)/d\tau}{(t-\tau)^{1/2}}d\tau\right], \tag{39}$$

where the subscript G denotes "Goodrich." In Eq. (39) the initial radius of the droplet has been set equal to 0.

Evaluation of the second term in the square brackets on the right-hand side of Eq. (38), making use of Eq. (16), yields 2α whereas the second term in square brackets on the right-hand side of Eq. (39) equals $(\sqrt{\pi}/16)\alpha$. Clearly, the α terms in these expressions are different. It is remotely possible that one of them is correct but, in the absence of rigorous evidence, there is no compelling reason to believe that

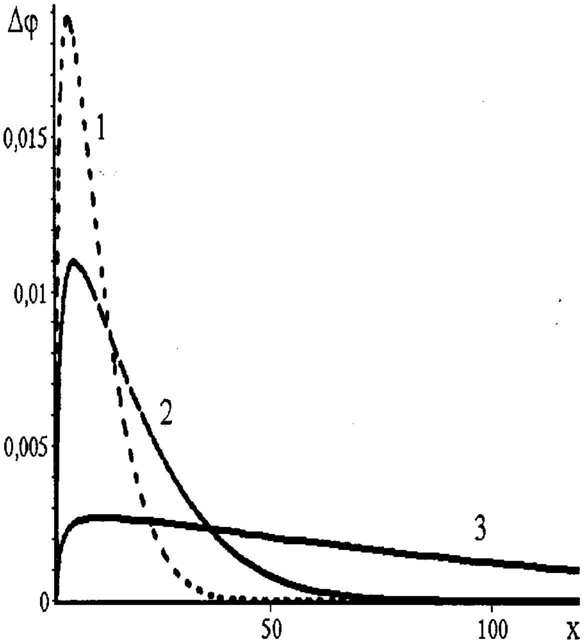

FIG. 1. The difference $\Delta\varphi$ between the values $\varphi(r,t)$ of the relative decrease in the vapor supersaturation found using solutions (3) and (28), respectively. Curves 1–3 correspond to $\alpha=0.05$, 0.025, and 0.005, respectively. x denotes the $r/R(t)$ ratio.

either is correct. Thus, including the terms linear in α, as a means of improving the approximations, must be considered unreliable.

For a theory of nucleation in the vapor proximate to a growing drop, knowledge of the profile of vapor concentration is important. Consequently, it is of interest to compare the profiles generated, respectively, by the conventional approach and the new approach. For this purpose, it is convenient to employ the following parameter:

$$\varphi(r,t)=\frac{n_0-n(r,t)}{n_0-n_\infty}. \tag{40}$$

At time t during the growth of the droplet, this is the relative decrease in vapor supersaturation at position r. In nucleation theory, the deviation of the nucleation rate from its value in the uniform vapor with the concentration n_0 can be expressed in terms of the quantity $\varphi(r,t)$.[13] This deviation is determined (at vapor supersaturations typical for homogeneous nucleation) by $\varphi(r,t)$, in the exponential factor in the expression for the nucleation rate, multiplied by a large dimensionless parameter having a magnitude between 40 and 50, approximately equal to the number of molecules in the condensation nucleus. It is therefore of special interest in regard to nucleation, to examine $\Delta\varphi$, the difference in the $\varphi(r,t)$'s obtained by the use of Eqs. (3) and (28), respectively, and it is especially interesting to examine this difference as a function of α.

Figure 1 is illustrative in this respect. In the figure, x is distance measured in units of the radius, $R(t)=\beta t^{1/2}$, of the growing droplet. In these units it is easily seen that $\varphi(r,t)$ the relative decrease in vapor supersaturation does not depend on time, independent of whether it is evaluated using Eqs. (3) or (28). The curves in Fig. 1 show the difference $\Delta\varphi$ between the values of the $\varphi(r,t)$ functions found using solutions (3) and (28), respectively. Curves 1, 2, and 3 correspond to $\alpha=0.05$, 0.025, and 0.005. They demonstrate a minor disparity between the conventional and new approaches. This disparity is however significant for a calculation of the nucleation rate in the vicinity of growing droplet.

We have presented above the treatment of the moving boundary problem assuming that the growing droplet is homogeneous and consists of condensate liquid only. Nevertheless, the whole approach can be extended to the growth of a spherical drop with a heterogeneous solid core in the course of heterogeneous vapor nucleation on wettable condensation nucleus. At this point, the case where the radius R_n of the solid condensation nucleus satisfies the inequality $R^2(t) \gg R_n^2$ [which is similar to Eq. (15)] is evident and does not require any change in formulas. The case of a large radius of the condensation nucleus, $R_n \leqslant R(t)$, can be described by the insertion of R_n as an initial droplet radius in the law of droplet radius growth [in Eqs. (2) and (16)]. To do this we just need to add a corresponding initial shift in time t in Eqs. (26) and (28). Another situation is the case of droplet formation on a partly wettable plane solid substrate where the spherical symmetry of the problem is disturbed. This case requires a distinct analysis.

In closing, it should be reiterated that the new approach, developed in this paper, for dealing with the moving boundary problem, has been supported only by a semiquantitative analytical argument and by the reasonable prediction of growth rate and material balance. For the future it remains desirable to develop a more rigorous analysis, possibly through a perturbative or variational approach utilizing the parameter α.

ACKNOWLEDGMENTS

This work was supported by the Russian Program "Russian Universities-Fundamental Research" (project UR.01.01.042), and by the United States National Science Foundation under NSF Grant No. CHE-0313563.

[1] H. Reiss and V. K. La Mer, J. Chem. Phys. **18**, 1 (1950).
[2] H. Reiss, J. Chem. Phys. **19**, 482 (1951).
[3] N. A. Fuchs, *Evaporation and Droplet Growth in Gaseous Media* (Pergamon, London, 1959).
[4] F. C. Goodrich, J. Phys. Chem. **70**, 3660 (1966).
[5] N. A. Fuchs and A. G. Sutugin in *Topics in Current Aerosol Research*, edited by G. M. Hidy and J. R. Brock (Pergamon, Oxgord, 1971), Vol. 2, p. 1.
[6] H. Reiss, J. R. Patel, and K. A. Jackson, J. Appl. Phys. **48**, 5274 (1977).
[7] D. Ilkovich, J. Chim. Phys. **35**, 129 (1938).
[8] P. Delahay and I. Trachtenberg, J. Am. Chem. Soc. **79**, 2355 (1957).
[9] P. Delahay and C. T. Fike, J. Am. Chem. Soc. **80**, 2628 (1958).
[10] J. G. Petrov and R. Miller, Colloid Polym. Sci. **255**, 669 (1977).
[11] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed. (Oxford University Press, New York, 1986).
[12] A. P. Grinin, F. M. Kuni, and I. A. Zhuvikina, Kolloidn. Zh. **64**, 769 (2002).
[13] F. M. Kuni and A. P. Grinin, Kolloidn. Zh. **46**, 460 (1984).