Growth of a single drop formed by diffusion and adsorption of monomers on a two-dimensional substrate

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We study a single, motionless three-dimensional (3D) drop growing by adsorption of diffusing monomers on a 2D substrate. A simple treatment based on a quasistatic approximation predicts that the radius of the drop increases as $[t/\ln(t)]^{1/3}$ in the long-time limit. By applying the method of matched asymptotic expansions we then confirm that the quasistatic approximation provides a dominant asymptotic behavior. We also show that the typical distance from the surface of the growing drop to the nearest surviving monomer scales as $[\ln(t)]^{1/2}$ and discuss the distribution function for that minimum distance.

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I. INTRODUCTION

When a vapor condenses onto a nonwetting substrate, the droplet pattern that emerges after the heterogeneous nucleation process evolves via several mechanisms, including the growth and the diffusion of individual droplets and the coalescence of contacting droplets. This and similar processes in which the coalescence of liquid droplets plays an important role are common in many areas of science and technology [1,2]. The kinetics of patterns formed by growing and coalescing droplets is an area of active recent research, both experimentally and theoretically [3–11]. To understand the kinetics of these processes several simplified models have been developed.

One such model [6,11] consists of a single, motionless three-dimensional (3D) drop formed by diffusion and adsorption of noncoalescing monomers on a 2D substrate. This model was introduced for a regime in which monodisperse diffusing droplets are widely spaced from one another and only the coalescence with large immobile growing trap is important. By using a *static* approximation for solving the diffusion equation, an approximate description of the long-time behavior has been reported recently by Steyer, Guenoun, Beysens, and Knobler [11]. The purpose of this paper is to present a more accurate description based on a *quasistatic* approximation and to show that this approximation provides a dominant asymptotic behavior.

While the spatial density of monomers surrounding a trap of *fixed* radius can be easily found by solving the diffusion equation subject to appropriate boundary conditions, the present problem involving a moving boundary requires a more complicated analysis. Moving boundary problems in the context of the diffusion equation or heat equation are often referred to as Stéfan problems [12–14]. The only exact solutions for these problems have been found by exploiting the existence of a similarity variable like $rt^{-1/2}$; see, e.g., [12–14] and references therein, and a recent study [15,16]. In the present problem one can find an exact scaling solution only when the dimensionality d of droplets is the same as the dimensionality of a substrate. Such a solution in one dimension has been derived by Harris [15]. It may be readily generalized to an arbitrary dimension d. However, the present problem of a 3D drop growing on a 2D substrate, as most Stéfan problems, may be treated only by approximate or numerical methods.

In Sec. II we define the model and write governing equations. In Sec. III we apply a quasistatic approximation for finding the spatial density of monomers surrounding the drop and calculating the radius of drop. In Sec. IV we derive a more subtle feature of the distribution of monomers—the nearest-neighbor distance from the drop. Then in Sec. V, by employing the method of matched asymptotic expansions, we give a more complete treatment of the problem and confirm that the quasistatic approximation indeed provides the dominant contribution to the long-time behavior.

II. GROWTH EQUATIONS

Consider an immobile growing drop, which will also be called a trap, to distinguish it from other droplets. Assume that the trap is located at the origin. The physical processes occurring during the coalescence event are very complicated. The resulting position of the trap after such an event is somewhere between its position before the coalescence and the position of the center of mass of the system of coalescing trap and droplet [5], but we will ignore these random, and small for large trap, factors. We assume that the trap is initially surrounded by the homogeneous density C_∞ of monodisperse droplets, monomers having the volume V and diffusing with the diffusion constant D. Then the density $C(r,t)$ of droplets at point r and at time t is described by the diffusion equation

$$\frac{\partial}{\partial t}C(r,t)=D\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}C(r,t) \quad \text{at } r\geq R \ , \tag{1}$$

subject to the initial and boundary conditions

$$C=C_\infty=\text{const} \quad \text{and } R=a \quad \text{at } t=0 \ , \tag{2}$$

$$C=0 \text{ and } V\left[2\pi r D\frac{\partial C}{\partial r}\right]=\lambda R^2\frac{dR}{dt} \text{ at } r=R \ , \quad (3)$$

where $R(t)$ is the radius of immobile growing trap, a is the initial radius, and λ is the nondimensional factor related to the contact angle. Note that the former condition in Eq. (3) is the appropriate adsorption boundary condition on the surface of the perfect trap while the latter condition in (3) is obtained from the mass conservation.

III. QUASISTATIC APPROXIMATION

We now employ the quasistatic approximation [17,18] for solving the Stéfan problem (1)–(3) with the moving boundary at $r=R(t)$. In this approximation one ignores the explicit time derivative in Eq. (1), and the time dependence in this equation is accounted for by a moving external boundary at $r=(Dt)^{1/2}$, in addition to the internal boundary at $r=R(t)$. Thus we must solve the Laplace equation in the active region $R(t)\le r\le (Dt)^{1/2}$ and then match this solution with the boundary values $C=0$ at $r=R(t)$ and $C=C_\infty$ at $r=(Dt)^{1/2}$. By a direct computation, we find

$$C(r,t)=2C_\infty\frac{\ln(r/R)}{\ln(Dt/R^2)} \ . \quad (4)$$

Substituting this into the growing rule (3) yields

$$4\pi D V C_\infty[\ln(Dt/R^2)]^{-1}=\lambda R^2\frac{dR}{dt} \ . \quad (5)$$

Solving (5) in the long-time limit gives

$$R(t)\simeq A\left[\frac{\tau}{\ln(\tau)}\right]^{1/3} , \quad (6)$$

where $A=(36\pi V/\lambda)^{1/3}$ and $\tau=C_\infty Dt$ is the dimensionless time.

IV. NEAREST-NEIGHBOR DISTANCES OF MONOMERS FROM THE TRAP

It is also possible to describe more subtle details of the growth process; e.g., the distance to the nearest surviving monomer from the trap. For an ideal spherical trap of *fixed* radius a, the density distribution function of that minimum distance has been discussed in a number of recent studies [18–20]. Following the lines of [18], we provide now a long-time asymptotic analysis of the density distribution function of the minimum distance of diffusing monomers from the *growing* trap. First, we compute $L_{\min}$, a characteristic minimum distance from the surviving monomer which is closest to the growing trap. We will use the criterion

$$\int_R^{R+L_{\min}} 2\pi r C(r,t)dr=1 \ . \quad (7)$$

By inserting the expression (4) into this criterion we obtain that in the long-time asymptotic limit the dimensionless characteristic minimum distance $\rho_{\min}=1+L_{\min}/R$ from the center of growing trap satisfies the transcendental equation

$$\rho^2\ln\rho-\frac{\rho^2-1}{2}=\frac{\ln(Dt/R^2)}{2\pi C_\infty R^2} \ . \quad (8)$$

It can be seen that $(\rho-1)$ tends to zero as t tends to infinity. Therefore, expanding the left-hand side of Eq. (8) and using (6), one can find the characteristic minimum distance at large times,

$$L_{\min}\simeq[\ln(\tau)/6\pi C_\infty]^{1/2} \ . \quad (9)$$

For an ideal trap of *fixed* radius a, the characteristic minimum distance behaves as

$$L_{\min}\simeq[\ln(Dt/a^2)/\pi C_\infty]^{1/2}\{\ln[\ln(Dt/a^2)]\}^{-1/2}$$

at large times [18], i.e., apart from a numerical factor, it differs from our result (9) only by the extremely slowly varying double logarithmic factor.

Consider now $p(L,t)$, the probability density function for distance $L_{\min}$. Applying the Hertz formula [21] in two dimensions, one has

$$p(L,t)=2\pi(R+L)C(R+L,t)\times\exp\left[-\int_R^{R+L}2\pi r C(r,t)dr\right] \ . \quad (10)$$

Substituting the quasistatic result (4) into (10) yields

$$p(L,t)=4\pi C_\infty R\frac{\rho\ln(\rho)}{\ln(Dt/R^2)}\times\exp\left[-\frac{2\pi C_\infty R^2}{\ln(Dt/R^2)}\left[\rho^2\ln\rho-\frac{\rho^2-1}{2}\right]\right] , \quad (11)$$

where $\rho=1+L/R$ and R is given by Eq. (6). This is the probability density function at large times.

Compute now the average distance of the nearest surviving particle from the surface of the trap,

$$\langle L\rangle=\int_0^\infty Lp(L,t)dL \ . \quad (12)$$

By inserting (11) into (12) we obtain the long-time asymptotic limit,

$$\langle L\rangle\simeq[\ln(\tau)/24C_\infty]^{1/2} \ . \quad (13)$$

We see that $L_{\min}$ given by (9) is not equal to the average distance $\langle L\rangle$ given by (13), though asymptotically these quantities scale in the same manner.

V. ASYMPTOTIC SOLUTION OF GROWTH EQUATIONS

Return now to the original problem of solving Eqs. (1)–(3) and discuss the validity of the quasistatic approximation. First, we compare our approach with another one that has been developed by Steyer *et al.* [11]. They used the stationary solution

$$C(r,t)=\frac{\Phi}{2\pi D}\ln\left[\frac{r}{R}\right] , \quad (14)$$

which obeys the absorbing boundary condition, $C(R,t)=0$, and the boundary condition of constant flux, $[2\pi r D(\partial C/\partial r)]|_\infty=\Phi$. Combining (3) and (14) one can find the following long-time behavior $R(t)=At^{1/3}$, with

$A=(3\Phi V/\lambda)^{1/3}$. Thus the asymptotic growth law predicted by the static approach differs from the quasistatic answer by a slowly varying logarithmic factor. Furthermore, one can observe a more serious deficiency of the static approach, namely, the appearance of an unknown constant Φ in Eq. (14) and in the expression for $R(t)$. In short, the inaccuracy of the static expression (14) for the density at all $r\geq R(t)$ leads to the inaccuracy of $R(t)$.

Observe now that the quasistatic expression (4) for the density also becomes inaccurate, but only at large distances from the trap. In fact, the quasistatic approximation (4) provides an accurate description at $R(t)\leq r \ll (Dt)^{1/2}$. The essential point is that for the determination of the radius of the trap we require the density distribution only near $r=R(t)$; see Eq. (3). Therefore the asymptotic growth law (6) is correct.

We confirm that the quasistatic approximation really provides the dominant contribution to the long-time asymptotic behavior at $R(t)\leq r \ll (Dt)^{1/2}$. We will do this by using the method of matched asymptotic expansions [22]. Applying this method one should divide the whole region $r\geq R(t)$ into the *inner* region, $R(t)\leq r\ll (Dt)^{1/2}$, and the *outer* region, $r\gg R(t)$. Then we will employ the *inner* variable $\eta=r/R(t)$ in the former region and the *outer* variable $\zeta=r(Dt)^{-1/2}$ in the latter region, expand the solution in the inner and outer regions, and finally match these expansions in the overlap region $R(t)\ll r\ll (Dt)^{1/2}$.

Introducing the inner variables (η,t) instead of (r,t) we rewrite the governing equation (1) as

$$R^2\frac{\partial C}{\partial t}-R\frac{dR}{dt}\eta\frac{\partial C}{\partial \eta}=D\frac{1}{\eta}\frac{\partial}{\partial \eta}\eta\frac{\partial C}{\partial \eta} \quad \text{at } \eta\geq 1 . \tag{15}$$

Because Eq. (15) does not contain any small parameter in an explicit form, we will seek its solution as a formal series:

$$C(\eta,t)=C_0(\eta,t)+C_1(\eta,t)+\cdots , \tag{16}$$

with $C_1(\eta,t)\ll C_0(\eta,t)$. This is the inner expansion mentioned above. Previous results (4) and (6) suggest that in the long-time limit terms on the right-hand side of Eq. (15) dominate compared to similar terms on the left-hand side. Assuming that this is valid in all approximations we find

$$\frac{1}{\eta}\frac{\partial}{\partial \eta}\eta\frac{\partial}{\partial \eta}C_0(\eta,t)=0 , \tag{17a}$$

$$\frac{1}{\eta}\frac{\partial}{\partial \eta}\eta\frac{\partial}{\partial \eta}C_1(\eta,t)=D^{-1}\left[R^2\frac{\partial}{\partial t}-R\frac{dR}{dt}\eta\frac{\partial}{\partial \eta}\right]C_0(\eta,t) \tag{17b}$$

in the zeroth and first approximations. Solving (17) we obtain

$$C_0(\eta,t)=B(t)\ln(\eta) , \tag{18a}$$

$$C_1(\eta,t)=\frac{R^2dB}{4Ddt}[\eta^2\ln(\eta)+1-\eta^2]+\frac{1}{4D}BR\frac{dR}{dt}(1-\eta^2) , \tag{18b}$$

with unknown functions $B=B(t)$ and $R=R(t)$. Observe that $C_1(\eta,t)$ is defined up to a solution to the homogeneous part of Eq. (17b), i.e., up to a term like $F(t)\ln(\eta)$, but one can involve such a term to the zeroth approximation.

We turn now to the outer region. In the variables $\zeta=r(Dt)^{-1/2}$ and t, the diffusion equation (1) becomes

$$t\frac{\partial C}{\partial t}=\frac{1}{\zeta}\frac{\partial}{\partial \zeta}\zeta\frac{\partial C}{\partial \zeta}+\frac{1}{2}\zeta\frac{\partial C}{\partial \zeta} . \tag{19}$$

Expanding the solution as above,

$$C(\zeta,t)=C_0(\zeta,t)+C_1(\zeta,t)+\cdots , \tag{20}$$

inserting (20) into (19), and solving resulting equations with the boundary condition $C(\zeta=\infty,t)=C_\infty$, yields

$$C_0(\zeta,t)=C_\infty , \tag{21a}$$

$$C_1(\zeta,t)=-B_1(t)\int_\zeta^\infty \xi^{-1}\exp(-\xi^2/4)d\xi . \tag{21b}$$

We determine now $B(t)$ and $B_1(t)$ by matching inner and outer solutions (18) and (21). To this end we will use the Van Dyke matching principle [22]. We rewrite (18a) in terms of the outer variable ζ, expand it in the long-time limit, and match with (21a). Thence we find $B(t)$:

$$C_0(\eta,t)=B\ln[\zeta(Dt)^{1/2}/R]$$
$$=B\ln[(Dt)^{1/2}/R]+\cdots=C_\infty ,$$

i.e.,

$$B(t)=C_\infty\{\ln[(Dt)^{1/2}/R(t)]\}^{-1} . \tag{22}$$

Similarly, we rewrite the inner solution $C_0(\eta,t)+C_1(\eta,t)$ in terms of the outer variable and the outer solution $C_0(\zeta,t)+C_1(\zeta,t)$ in terms of the inner variable, expand these solutions, match them, and finally derive $B_1(t)=B(t)$.

Thus, in the zeroth approximation given by Eqs. (18a) and (22), we have reproduced the previous quasistatic result (4). In particular, the radius of the trap in the zeroth approximation satisfies (5) and, consequently, $R(t)$ increases as $[t/\ln(t)]^{1/3}$ and $B(t)$ decreases as $[\ln(t)]^{-1}$ at $t\gg 1$. Having established these asymptotics one sees that

$$C_1(\eta,t)/C_0(\eta,t)\simeq t^{-1/3}[\ln(t)]^{-2/3}\ll 1 ,$$

$$C_1(\zeta,t)/C_0(\zeta,t)\simeq[\ln(t)]^{-1}\ll 1 ,$$

thus confirming that the necessary conditions for applying the formal series (16) and (20) are satisfied. In the first approximation the radius of the trap may be found from the equation

$$2\pi DV\left[B-\frac{R^2dB}{4Ddt}-\frac{1}{2D}BR\frac{dR}{dt}\right]=\lambda R^2\frac{dR}{dt} , \tag{23}$$

with $B(t)$ given by (22). A tedious analysis then shows that the radius behaves as $R(t)=R_0(t)-2\pi VC_\infty[\lambda\ln(\tau)]^{-1}$ at $t\gg 1$, where $R_0(t)$ is the zeroth approximation, i.e., a solution of Eq. (5).

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