

## Droplet growth and coarsening during heterogeneous vapor condensation

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A theoretical description of droplet growth and coarsening is presented for vapor condensing onto a partially wetting surface. Both individual droplet growth and coalescences are included in the description. The coupling of these growth mechanisms results in two characteristic lengths. The radii of *individual* droplets, nucleated onto the surface, increase as a power of time:  $R \sim t^m$ . Diffusion-limited growth on the surface leads to a characteristic exponent  $m = \frac{1}{4}$ . As a result of coalescences, however, the *average* droplet radius grows with an exponent of  $3m$ . Further predictions of the theory are also discussed.

### I. INTRODUCTION

The dynamics of a first-order phase separation is an important example of the growth of order in a nonequilibrium system. The process is typically initiated by a rapid change (quench) of a thermodynamic variable (e.g., temperature) such that the system is brought from a one-phase equilibrium state to a nonequilibrium state inside the coexistence curve. Following the quench, spatial inhomogeneities in the order parameter develop into domains, which then grow with time in a highly nonlinear manner. Recently interest has focused on the role various length scales play in the pattern formation. For systems with no impurities (i.e., homogeneous nucleation and spinodal decomposition), there is considerable evidence of the emergence of a dominant length (the average domain size), leading to an evolving morphology which scales with time.<sup>1</sup> The time dependence of this length and the extent of scaling have become central issues. However, relatively little is known about the degree to which similar behavior occurs during heterogeneous nucleation,<sup>2</sup> where phase separation is induced by a substrate.

For the case of liquid-vapor phase separation, a partially wetting surface can serve as a site for nucleation and growth of fluid droplets from a (thermodynamically) metastable vapor. The mist formed when one breathes on a cold surface is a common example of this phenomenon (i.e., "breath figures"). Recent experiments<sup>3</sup> reveal the existence of three stages to this phase-separation process. Initially there is a time regime of rapid creation and growth of small nuclei on the substrate surface. This nucleation stage is followed by a period of uniform coarsening of fluid droplets, which are large compared to the embryos of nucleation. During the coarsening stage, the radii of *individual* fluid droplets and the *average* droplet radius form two characteristic length scales which have different temporal behaviors. In particular, while both lengths grow as a power of time, the exponent describing individual droplet growth is significantly smaller than the exponent corresponding to the growth of the average droplet radius. Finally, gravitational effects become important in the late stages of growth.

In this paper a theoretical description of the coarsening stage of surface-induced phase separation is presented. The purpose of the work is to outline a framework for understanding the process of pattern formation in a system with coupled growth mechanisms. It is shown that the coupling can lead to more than one characteristic length scale in the problem. The growth of individual droplets is considered in the limit where coarsening is dominated by dynamics on the surface. A model of diffusion-limited droplet growth is developed from a mean-field boundary-layer approximation. Using asymptotic techniques, it is shown that individual droplets grow with an exponent of  $\frac{1}{4}$ . A rate equation is used to describe the coalescence of droplets. A scaling analysis reveals that, in general, the average droplet radius grows with an exponent three times as large as the exponent describing individual droplet growth. Further predictions of the theory are also discussed and compared with experiments and computer simulations.

### II. GROWTH EQUATIONS

A typical experimental setup for studying breath figures<sup>3</sup> employs a stream of saturated water vapor which is directed towards a glass slide. The glass is chemically treated to produce a partially wetting surface. The temperature of the slide is less than the vapor temperature so that the cold surface induces condensation of the water. The term "breath figures" refers to the evolving pattern of condensed water droplets that forms on the slide.

Two modes of growth are inherent to the system. Individual drops grow as a result of the impingement of water from their environment. This growth is characteristic of the details of the system studied, and will depend on factors such as the treatment of the surface, the temperature, and the volumetric flow rate. When two growing drops come into contact, they coalesce to form a larger drop. The coalescence mechanism is a second, much faster growth process. For immobile drops, coalescences result primarily from geometrical constraints. Figure 1 shows schematically how the two processes are coupled. In this figure the radius of a single droplet is plotted as a function of time. The plateaus correspond to the growth of the droplet in isolation, while the intermittent jump

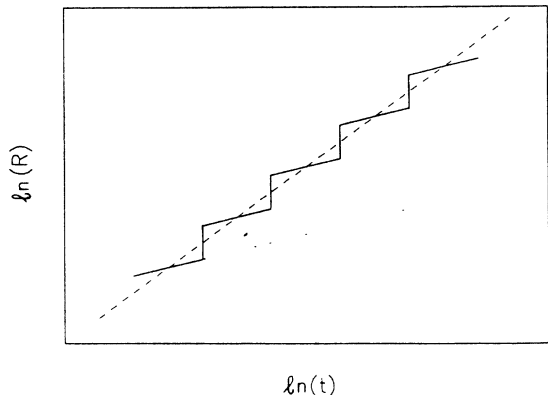


FIG. 1. Radius of a droplet as a function of time is plotted as a solid line. Dotted line corresponds to a growth exponent of  $\frac{1}{4}$ ; dashed line corresponds to an exponent of  $\frac{3}{4}$ .

discontinuities represent coalescences with neighboring drops in the system.

Although intrinsically coupled, the modes can be differentiated by virtue of the time scales involved. We define  $\tau_M$  as the average time between droplet coalescences. When the growth of a drop is considered over a time scale much less than  $\tau_M$ , the impingement of water from the environment is the dominant growth process. For time scales much greater than  $\tau_M$  the coalescence mechanism is important. Based upon this separation of time scales, a self-consistent description of the system is developed in the following sections.

#### A. Individual droplet growth

The growth of individual droplets is mediated by the flux of molecules from the environment. Growth mechanisms can be identified according to the process whereby molecules are transported to the droplet. The direct molecular flux from the saturated vapor stream can prevail for large volumetric flow rate and weak monomer adsorption. This limit is discussed in Ref. 3 where it is shown that individual droplet radii grow as a linear function of time. (However, there is evidence that this mechanism is suppressed for the case of water, either as a result of high surface temperature or strong reflectivity of the polar molecules.)<sup>4</sup> When the surface mobility is large the two-dimensional motion of molecules on the substrate can determine the growth dynamics. In this section a theory of droplet growth is developed for the latter case, where the dynamics of the system is dominated by diffusion-limited growth. Attention is restricted to the case that the diffusion of monomers controls the dynamics. However, the nature of the diffusing species is not important in determining the asymptotic growth exponents.<sup>5</sup>

It is assumed that the monomers undergo diffusive motion in a two-dimensional layer, parallel to the surface of the glass slide. Upon contact with a drop, they are instantaneously absorbed. The absorption of monomers leads to an increase in the size of the drop through mass

conservation. In this sense, the growth of drops is a diffusive process, which has formal analogies to diffusion-limited reaction theory.<sup>6</sup> We define  $n(\mathbf{r}, t)$  as the concentration of adsorbed monomers at position  $\mathbf{r}$  on the glass slide at time  $t$ . This quantity, defined only in the matrix surrounding the droplets, obeys a diffusion equation of the form,

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D \nabla^2 n(\mathbf{r}, t) + J, \quad (1)$$

where  $D$  is the diffusion coefficient for the matrix. The quantity  $J$  represents the rate of incorporation of monomers on the slide from the third dimension. It is assumed that this process saturates at some density  $n_0$ , which will depend on the incoming volumetric flow rate. The drops themselves form diffusion sinks for the two-dimensional flux of monomers.

In order to understand the nature of the growth process it is insightful to consider the dynamics of a single drop, in the absence of competition from neighboring ones. The drop is assumed to have a spherical cap shape as shown in Fig. 2. If the contact angle is the same for all drops, then the morphology is characterized by the radius  $R$  of the circle covered by the droplet on the slide. We choose a coordinate system with origin at the center of the circle, and assume circular symmetry of the diffusion field about the drop. Since the drop forms an absorber, the concentration of monomers at its perimeter satisfies

$$n(R, t) = 0. \quad (2)$$

Sufficiently far from the drop, the field approaches the saturation value,

$$n(\infty, t) = n_0. \quad (3)$$

Concentration gradients in the neighborhood of the droplet create a flux of monomers on the two-dimensional glass slide. The flux, in turn, feeds the growth of the droplet. The rate of increase of the droplet volume is related to the total flux of monomers at the perimeter of the droplet by mass conservation,

$$\rho_w \frac{dV}{dt} = 2\pi R \phi, \quad (4)$$

where  $V$  is the volume of the drop and  $\rho_w$  is the number density of water. The flux  $\phi$  is related to the gradient of the diffusion field normal to the droplet perimeter,

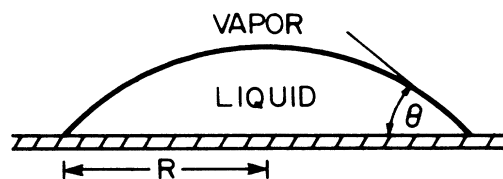


FIG. 2. Geometry of a droplet.

$$\phi = D \left. \frac{\partial n(r,t)}{\partial r} \right|_R. \quad (5)$$

By using the geometrical relationship  $V = 2\pi R^3/3\Gamma(\theta)$ , Eq. (4) can be rearranged to yield an equation of motion for the droplet radius,

$$\frac{dR}{dt} = \rho_w^{-1} \Gamma(\theta) \frac{\phi}{R}, \quad (6)$$

where

$$\Gamma(\theta) = 2 \sin^3 \theta / (\cos^3 \theta - 3 \cos \theta + 2)$$

is related to the contact angle  $\theta$ .

There is no general solution to the moving boundary problem of diffusion limited growth, as defined by Eqs. (1)–(6). Successful schemes for handling the problem rely on developing an approximation<sup>7–10</sup> for the two-dimensional flux  $\phi$ . For the case that the growth of the droplet perimeter on the glass surface is slow compared to the dynamics of the diffusion field, one can solve for the growth of the droplet by assuming that a steady-state concentration profile is maintained.<sup>7,8</sup> In this quasistatic approximation, the time derivative in Eq. (1) is set to zero. For the opposite case of rapid droplet growth, it is inappropriate to assume that the diffusion field over all space can react instantaneously to the changes in the boundary conditions. In this limit, a boundary-layer approximation has been developed,<sup>7,9,10</sup> wherein gradients in the diffusion field are confined to a small region surrounding the growing drop.

For breath figures, the description of monomeric diffusion is complicated by the fact that droplets are in competition.<sup>11–14</sup> Thus the flux of monomers into a given droplet depends on the distribution of droplets in its neighborhood. The long-ranged nature of the diffusion field in two dimensions forces a careful consideration of droplet competition from the outset.

In this paper a mean-field approximation is invoked, whereby competition between neighboring drops is replaced by an “effective medium.” In the mean-field picture a single drop grows as a result of the diffusion-limited flux of monomers from the effective medium. A new length scale is introduced into the problem in the form of a screening length, which can be defined as the average distance from the perimeter of a drop over which the diffusion field is affected by the presence of the drop. The full many-body problem reduces to the consideration of an isolated drop in the matrix of an effective medium. The diffusion-limited growth of the isolated drop can be solved using the approximation schemes discussed above. The screening length is related to averages over the droplet distribution in a self-consistent fashion.

In the effective medium, monomers diffuse through a collection of sinks (growing droplets) and sources (flux of new monomers). The quantity  $n_0$  is defined as the average concentration established in the medium. It will be time independent when the rate of incorporation of new monomers balances, on average, the rate at which monomers are removed by the growing droplets. (This balance is discussed in more detail in Sec. III.) The diffusion of

monomers in the effective medium is then a mass-conserving process.

As a result of rapid droplet growth, gradients in the diffusion field surrounding a given droplet are limited to a narrow boundary layer. It is assumed that, in this region, the concentration profile varies linearly with radial distance from the drop’s perimeter as shown in Fig. 3. The flux of monomers into a droplet can then be cast in the form

$$\phi = \frac{Dn_0}{\xi}. \quad (7)$$

This equation serves to define the screening length  $\xi$ , which is an average property of the effective medium. Substituting into (6) gives

$$\frac{dR}{dt} = D\rho_w^{-1} \Gamma \frac{n_0}{R\xi}. \quad (8)$$

The dynamics of  $\xi$  is established from mass conservation. In particular, there is a monomer deficit associated with the boundary layer. It is convenient to introduce the quantity  $h$ , which measures the depletion of monomers in the boundary layer,

$$h = \int_R^\infty dr (n_0 - n) = \pi n_0 R \xi. \quad (9)$$

The last equality is valid provided  $\xi \ll R$  (see Sec. III). The depletion zone arises from the absorption of monomers at the perimeter of the droplet. On average, the number of molecules entering the growing drops equals the amount leaving the boundary layers. This restriction leads to the relation,

$$\int dR \psi(R,t) \frac{dh}{dt} = \rho_w \int dR \psi(R,t) \frac{dV}{dt}, \quad (10)$$

where the droplet distribution function  $\psi$  has been introduced. This function is defined such that  $\psi(R,t)dR$  is the number of drops with radius between  $R$  and  $R + dR$  per unit surface area at time  $t$ . Equation (10) relates the boundary layer to averages over the entire drop distribu-

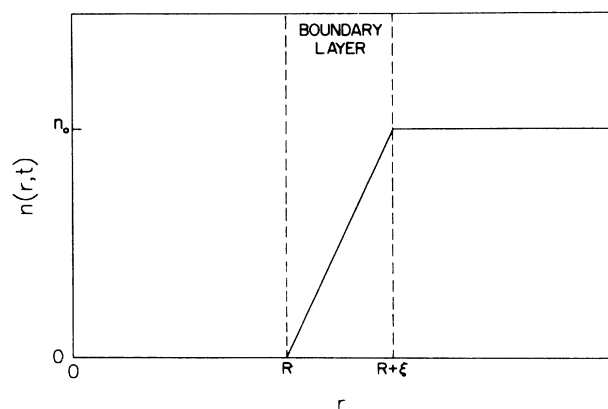


FIG 3. Concentration profile in the vicinity of a growing droplet. The abscissa corresponds to the radial distance from the center of the droplet.

tion, and thus couples the growth of an individual drop to the coalescence mechanism.

The equations can be rewritten in terms of dimensionless variables using the following definitions:

$$\bar{R} = n_0^{1/2} R ,$$

$$\bar{\xi} = n_0^{1/2} \xi ,$$

$$\tau = 4Dn_0 t .$$

Equation (8) for individual droplet growth becomes

$$\frac{d\bar{R}}{d\tau} = \frac{\alpha}{\bar{R}\bar{\xi}} , \quad (11)$$

where

$$\alpha = \frac{n_0^{3/2} \Gamma}{4\rho_w} .$$

In order to establish the time dependence of  $\xi$ , it is convenient to rearrange (10) in the form

$$\bar{\xi} \frac{d\bar{\xi}}{d\tau} + \alpha \langle \bar{R} \rangle^{-1} \langle \bar{R}^{-1} \rangle \bar{\xi}^{-\frac{1}{2}} = 0 , \quad (12)$$

where we have used  $V = 2\pi R^3/3\Gamma$ , and have substituted for  $d\bar{R}/d\tau$  from (8). The angular brackets in Eq. (12) denote an average over the droplet distribution function, such that

$$\langle f(\bar{R}) \rangle = \frac{\int f(\bar{R}) \psi d\bar{R}}{\int \psi d\bar{R}} \quad (13)$$

for an arbitrary function  $f$ . The method of dominant balance<sup>15</sup> can be used to extract the asymptotic behavior of  $\bar{\xi}$ , with the result

$$\bar{\xi} \sim \tau^{1/2} + O(\tau^{-1/2} \ln(\tau)) , \quad (14)$$

provided  $\langle \bar{R} \rangle^{-1} \langle \bar{R}^{-1} \rangle \bar{\xi}$  tends to zero asymptotically. This limit is obtained because of the rapid dynamics of coalescence as discussed in Sec. II B. Substituting (14) into (11) generates

$$\bar{R}(t) \sim 2\alpha^{1/2} \tau^{1/4} \quad (15)$$

for large  $\tau$ . Thus  $R$  and  $\xi$  grows as powers of time asymptotically, with exponents of  $\frac{1}{4}$  and  $\frac{1}{2}$ , respectively.

## B. Coalescence

The droplets are constrained by the geometry of the surface of the slide. Since all drops grow as a result of the flux of monomers, neighbors will come into contact with one another. Coalescence is the process whereby droplets whose surfaces are in contact merge to form a single larger droplet.<sup>16–18</sup> During this process the average droplet radius increases, while the number of drops is reduced.

An important element of a theory of coalescence is the droplet distribution function  $\psi(\bar{R}(\tau), \tau)$ . In defining  $\psi$ , the time-dependent growth of  $\bar{R}$  due to diffusion has been included such that, without coalescence,  $\psi$  does not change with time (i.e., the  $R$  coordinates “move” with the

growing drops). It is assumed that when two drops of size  $\bar{R}_1$  and  $\bar{R}_2$  touch, they instantaneously coalesce. Further, triple and higher multiple coalescences are replaced by independent, sequential binary coalescences. Then, the probability distribution function obeys a Smoluchowski-type rate equation:

$$\dot{\psi} = \int P(\bar{R}_1, \bar{R}_2) \delta((\bar{R}_1^3 + \bar{R}_2^3)^{1/3} - \bar{R}) d\bar{R}_1 d\bar{R}_2 - \int P(\bar{R}_1, \bar{R}) d\bar{R}_1 . \quad (16)$$

The time derivative is defined over a time scale  $\Delta\tau \gg \tau_M$ , which is large compared to the mean time between coalescences, yet small compared to the time scales of the experiment, i.e.,

$$\dot{\psi} = \frac{\psi(\bar{R}(\tau + \Delta\tau), \tau + \Delta\tau) - \psi(\bar{R}(\tau), \tau)}{\Delta\tau} . \quad (17)$$

The factor  $P(\bar{R}_1, \bar{R}_2)$  represents the probability of coalescence of two clusters of size  $\bar{R}_1$  and  $\bar{R}_2$  per unit area per unit time.

The first term on the right-hand side of (16) is a gain term representing the rate at which two droplets coalesce to form one of size  $R$  during the time interval  $\Delta\tau$ . The second term represents the loss of drops of size  $R$  due to their coalescence with other drops in the system. The coalescence rate is related to the probability of overlap of two drops. For a homogeneous droplet distribution, we can write

$$P(\bar{R}_1, \bar{R}_2) = K(\bar{R}_1, \bar{R}_2) \psi(\bar{R}_1) \psi(\bar{R}_2) . \quad (18)$$

Here the kernel  $K$  is equivalent to a reaction cross section. Equation (18) does not account for the effects of spatial correlations among the coalescing droplets.

The kernel reflects the dynamics which cause droplets to come into contact. In conventional reaction theory<sup>6</sup> coalescences result from the collision of diffusing particles. However, in the system considered here, the droplets are essentially immobile. Instead, collisions result from the increased surface area covered by the growing droplets. The kernel is given by

$$K(\bar{R}_1, \bar{R}_2) = 2\pi(\bar{R}_1 + \bar{R}_2)(\dot{\bar{R}}_1 + \dot{\bar{R}}_2) . \quad (19)$$

The relative velocity of approach of the two droplets,  $\dot{\bar{R}}_1 + \dot{\bar{R}}_2$ , must take into account all growth mechanisms relevant to the time scale  $\Delta\tau$ .

The instantaneous droplet coalescences are volume conserving. Consequently, it is only through the growth of individual droplets (between coalescences) that the total volume of condensed fluid increases. We consider the general case that individual droplets grow as a power of time, with an exponent  $m$ . (For diffusion-limited growth,  $m = \frac{1}{4}$  as shown in Sec. II A.) A time-invariant quantity can be constructed by rescaling the volume of each drop according to the growth law. Namely,

$$\int [\tau^{-m} \bar{R}(\tau)]^3 \psi(\bar{R}(\tau), \tau) d\bar{R}(\tau) = C , \quad (20)$$

where the constant  $C$  is independent of time.

Equations (16)–(20) describe droplet coalescence in the

system. Although a general solution to these equations is elusive, the asymptotic behavior of various quantities can be established by means of a time-scaling analysis.<sup>14,16-18</sup> The analysis involves the elimination of explicit time dependence from the dynamical equations. In the process, the late stage growth of the length scales in the problem can be extracted. The scaling (or similarity) analysis centers around the ansatz that the distribution function assumes a form,

$$\psi(\bar{R}(\tau), \tau) = \tau^{-y} \psi_0(z), \quad (21)$$

where  $z = \bar{R}(\tau)\tau^{-x}$ , and the exponents  $x$  and  $y$  are to be determined. Scaling is an assumption of self-similarity in the evolution of the morphology.

An immediate consequence of the scaling ansatz is a power-law growth of the average radius. Specifically, the scaling form of the distribution function leads to

$$\langle \bar{R} \rangle = a\tau^x, \quad (22)$$

where  $a$  is a time-independent normalization factor,

$$a = \frac{\int z \psi_0(z) dz}{\int \psi_0(z) dz}. \quad (23)$$

From Eq. (22) it is clear that  $x$  is the exponent which characterizes the growth of the average radius.

The exponents  $x$  and  $y$  are related through the equation for coalescence. The relationship is manifested by eliminating the implicit time dependence of  $R$  in favor of the scaled variable  $z$ . The time rate of change of the radius, when considered over the time scale  $\tau_M$ , assumes the form

$$\dot{R} = \frac{R(\tau + \Delta\tau) - R(\tau)}{\Delta\tau} \sim \tau^{x-1} z. \quad (24)$$

Substituting (21) and (24) into (16) generates an integral equation for  $\psi_0$ . In order for  $\psi_0$  to be time independent, which is the hallmark of scaling, the explicit time dependence must be eliminated from the equation. This occurs when the exponents satisfy

$$y = 3x. \quad (25)$$

Further, the partial integral equation of coalescence is reduced to an ordinary integral equation of the form,

$$\begin{aligned} \psi_0(z) = & -\frac{2\pi}{3} \int dz_1 \int dz_2 \psi_0(z_1) \psi_0(z_2) (z_1 + z_2)^2 \\ & \times \delta[(z_1^3 + z_2^3)^{1/3} - z] \\ & + \frac{2\pi}{3} \int dz_1 \psi_0(z_1) \psi_0(z) (z_1 + z)^2. \end{aligned} \quad (26)$$

The solution to this equation is the scaling form of the droplet distribution function.

A relationship between the radial growth of individual droplets and the growth of the average droplet radius is implicit in Eq. (20). Substituting the scaling form (21) into (20) and using (25) yields,

$$\tau^{x-3m} \int dz \psi_0 z^3 = C.$$

Time independence of the coefficient  $C$  requires

$$x = 3m. \quad (27)$$

Equation (27) shows that the average droplet radius grows with an exponent three times as large as the exponent describing the growth of an individual droplet. This is a general result which is independent of the mechanism for individual droplet growth.

The first few moments of the distribution function give important information about the growth process. It is these averaged quantities which are usually measured experimentally. The temporal dependence of these moments can be determined in a straightforward manner. For example, the zeroth moment is defined as

$$N(\tau) = \int dR(\tau) \psi(R(\tau), \tau).$$

This quantity measures the total number of droplets per unit area. Using Eq. (21) leads to the result

$$N(\tau) \sim \tau^{-2x} \int dx \psi_0(z). \quad (28)$$

Thus the number of droplets in the water condensation experiment<sup>3</sup> decreases as a power of time with an exponent of  $\frac{3}{2}$ . From the second moment it is evident that the area covered by the growing droplets is time independent:

$$A = \int dR(\tau) \psi(R(\tau), \tau) R^2(\tau) \sim \int dz \psi_0 z^2. \quad (29)$$

Constant surface coverage of the droplets is an important signature of scaling in the growth.

### III. DISCUSSION

A theoretical description of droplet evolution during heterogeneous phase separation necessitates the coupling of growth and coalescence mechanisms. The radii of individual droplets on the surface increase with time as a result of vapor condensation from the third dimension. This growth is influenced by the details of the experiment. For the case that the two-dimensional diffusive flux is the dominant growth mechanism, we have shown that individual droplets grow as  $t^{1/4}$ . This law is derived from a mean-field analysis, wherein a screening length  $\xi$  accounts for interdroplet interactions. Equation (14) shows that the screening length grows as  $t^{1/2}$ . The growth law results from the fact that  $\xi$  is a diffusion length. Because of the rapid growth of the average radius, it is clear that

$$\frac{\xi}{\langle R \rangle} \sim t^{-1/4}. \quad (30)$$

For large times, the screening length is small compared to the droplet radii, so that the approximation leading to Eq. (9) is valid. (Note, it is the *average* droplet radius which ultimately determines the timescale for growth, as illustrated in Fig. 1.)

It is interesting to compare this result with the Lifshitz-Slyosov theory of *homogeneous* droplet coarsening.<sup>1,8,14</sup> For the latter, the average droplet radius grows more slowly than  $t^{1/2}$ . Thus a boundary-layer theory will eventually break down because the condition  $\xi \ll R$  can-

not be maintained. As a result, the dynamics of the diffusion field become slaved to the average radius, resulting in a growth exponent of  $\frac{1}{3}$  for both. For the *heterogeneous* growth described in this paper, the coupling of coalescence to the diffusion-limited growth of individual droplets dramatically increases the growth of the average droplet radius. The rate-determining quantity for droplet growth then becomes the diffusion length.

Implicit in the mean-field analysis is the requirement that the rate of introduction of monomers onto the surface is balanced by the rate at which the monomers are incorporated into the growing droplets, when averaged over the entire droplet distribution. Since monomers are adsorbed only in the depletion zone in the immediate neighborhood of the growing droplets, the flux rate will be proportional to the total area covered by the boundary layers,

$$J = 2\pi F \int dR \psi R \xi . \quad (31)$$

The coefficient  $F$  is the average adsorption rate, which depends on the volumetric flow rate of the gas and the surface properties of the slide. The rate of change of the number of molecules in the growing drops is given by

$$\dot{n}_{\text{tot}} = \rho_w \left( \frac{2\pi}{3\Gamma} \right) \frac{d}{dt} \int R^3 \psi dR . \quad (32)$$

Substituting for the asymptotic solutions yields the result that both  $J$  and  $\dot{n}_{\text{tot}}$  are proportional to  $\tau^{-1/4}$ . Thus the temporal dependences balance, as required.

The coalescence of droplets leads to a faster growth of the average droplet radius. This mechanism can be described by a rate equation for the droplet distribution function which assumes a particularly simple form in the reference frame of the growing droplets. A similarity solution exists which yields a growth exponent  $3m$ , where  $m$  is the exponent describing the growth of individual droplets. The relationship between the two exponents is a consequence of the geometrical constraints of three-dimensional droplets growing on a two-dimensional surface.

The process of vapor condensation on a cold surface is a complex phenomenon. In this paper a simplified theory has been presented which allows only two growth mechanisms, namely, diffusion-limited surface dynamics and droplet coalescence. Although restricted in scope, this

analytic approach to droplet growth compares favorably with recent experiments and computer simulations. For example, in studying the growth of breath figures, Beysens and Knobler<sup>3</sup> measured an exponent of  $0.23 \pm 0.05$  for individual droplet growth, while the average droplet radius was characterized by an exponent of  $0.75 \pm 0.05$ . During the pattern growth, the average surface coverage remained constant, consistent with the assumption of dynamical scaling. The relationship between individual droplet growth and the average droplet radius has also been verified in numerical simulation studies.<sup>3</sup>

It should be noted that the exponent  $m$  (which describes individual droplet growth) depends, to a large extent, on the transport mechanism whereby the vapor molecules reach the droplets. Low volumetric flow rate and high surface mobility are important characteristics of a system where diffusion will dominate. In general, however, diffusion-limited growth is only one of a variety of mechanisms that may contribute to the dynamics of individual droplets. (We have not considered the role of surface impurities and thermal transport, for example.) In contrast, the relationship between  $m$  and  $x$  (the exponent for the average radius) emerges from the geometry, and is a universal result.

#### IV. CONCLUSION

The droplet patterns formed when a vapor condenses on a surface has been described analytically in terms of the interplay of two growth mechanisms. The radii of individual droplets grow as a power of time, with an exponent of  $\frac{1}{4}$ . This growth is the result of diffusion on the surface. Droplet coalescences cause the average droplet radius to grow with an exponent of  $\frac{3}{4}$ . The predictions of the theory are in agreement with recent experiments on the condensation of water on a partially wetting surface.

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