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Scaling description for the growth of condensation patterns on surfaces

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The growth of a droplet pattern condensing on a surface (e.g., breath figures) is analyzed for the case of arbitrary dimensionality. The growth of a droplet occurs through a two-step process: (i) continuous growth by condensation on its surface and/or on the substrate and (ii) coalescence with neighboring droplets. As long as the one-droplet growth remains scale invariant, the growth of the entire pattern is shown to be self-similar in time and very general growth laws can be deduced, whose exponents are functions only of the dimensionality of the space of the droplets, and of the condensing substrate. In particular, for the case of three-dimensional droplets condensing on a plane substrate (breath figures), the growth exponent of a single droplet should be $\frac{1}{3}$, whereas the exponent corresponding to a mean droplet, averaged over the pattern, should be unity. Comparison with experiment is performed and possible deviations from the predictions are considered.

I. INTRODUCTION

The condensation of fluids on cold surfaces is an aspect of phase transitions experienced daily. The importance of condensation in thermal technology (heat exchangers, condensers, etc.) motivated an early engineering interest,[1] but fundamental studies are surprisingly scarce.[2] Recently, new experiments have been described[3,4] in which detailed investigations were made of the growth of breath figures produced by blowing nitrogen saturated with water vapor onto a cold glass surface. In the "incomplete wetting" case (silanized glass), a rather complex dynamic behavior was observed, including the following four different regimes.

(i) At very short times ($t < 1s$), a furious and complex activity is observed, which seems to depend significantly on experimental conditions. The time and size resolution of the experimental setup did not permit a detailed study of this regime.[5]

(ii) An "intermediate" regime is reached rapidly, and persists during two or three decades of time. In this regime, one can distinguish distinct growth mechanisms which coexist. The first one is a continuous growth due to condensation from the supersaturated vapor. The absence of new nucleated droplets between drops in this regime suggests that all the vapor molecules reaching the surface are efficiently collected by the preexisting droplets. The centers of the droplets do not move during this process, in contrast to the second mechanism, which consists of a fast, intermittent coalescence of neighboring droplets. The mean droplet radius $\bar{\rho}$ seems to follow a power law,

$$\bar{\rho} \sim t^{\mu_0} \text{ with } \mu_0 \simeq 0.75 \ , \tag{1}$$

whereas the apparent exponent for individual droplet growth is $\mu_a \sim 0.23$. (A rigorous definition for this apparent exponent will be given in Sec. V.)

Other important features of the intermediate regime are the development of a unimodal distribution of droplet sizes with very stable polydispersity and surface coverage.

(iii) At longer times ($t \gtrsim 10^2 - 10^3$ s) "new" small droplets appear on the surface between the large "old" ones, and the pattern evolution becomes more complex.

(iv) Finally, the droplets lose their hemispherical shape and/or begin to flow because of gravity.

In the present paper we report preliminary theoretical investigations of the growth of condensation patterns on nonwetting surfaces. We restrict ourselves to regime (ii), which contains many important features of the general dynamics, and is relatively simpler and better characterized than the others. Since dimensionality is very important here, we develop a theory for arbitrary dimensions, considering the experiment discussed above as a particular case [three-dimensional (3D) objects on a 2D substrate). We also make predictions for another experimentally available combination of dimensionalities, 3D droplets on a quasi-1D thread. To our knowledge, the growth of droplet patterns on threads has never been studied quantitatively. Apart from their practical interest for coating, such studies may help clarify the dimensional aspects of our theoretical approach. Last but not least, very convincing realizations, such as the patterns of morning dew on spider webs, should be readily available.

II. CONDENSATION GROWTH

The primary growth process is continuous condensation. The rate can be expressed generally as

$$dn_i(t)/dt = A_{\text{eff}}\varphi_V \ , \tag{2}$$

where n_i is the number of moles of water (or, more generally, condensing fluid) in the droplet i, A_{eff} is the effective collection surface of the droplet, and φ_V is the flux of vapor molecules per unit area on the surface. To keep the problem tractable, we suppose that the flux is small enough (and/or the thermal conductivity high enough) to ensure a constant and uniform temperature in the ensemble of substrate plus droplets, i.e., a thermal steady state is reached during regime (ii). We also suppose steady-state hydrodynamics, i.e., φ_V does not vary with time and may change with the position only on scales much greater than $\bar{\rho}$. These assumptions seem to be reasonable for laminar flows, but more complicated situations could be encountered when the hydrodynamics of the incipient gas involves length scales comparable to the droplet size.

For a droplet growing on a thread, condensation on the thread becomes negligible as soon as $\bar{\rho} > d$, the diameter of the thread. For a sufficiently thin, nonwetting thread, we can assume that the droplets are spherical and that condensation between droplets on the thread is negligible in regime (ii).

From Eq. (2), with ρ_i the radius of droplet i,

$$dn_i/dt \simeq 4\pi\rho_i^2\varphi_V \ . \tag{3}$$

Volume conservation requires

$$n_i V_W = 4\pi\rho_i^3/3 \ , \tag{4}$$

where V_W is the molar volume of water, and leads to the growth law,

$$\rho_i - \rho_{i,0} = V_W\varphi_V(t - t_0) \ . \tag{5}$$

Here $\rho_{i,0}$ is the radius of droplet i at time t_0.

For a droplet growing on a surface on which the wetting is incomplete (e.g., contact angle $\pi/2$), the surface area and volume of the droplet are $2\pi\rho_i^2$ and $2\pi\rho_i^3/3$, respectively. Generalization to other contact angles θ would be straightforward, and it would introduce only θ-dependent prefactors. However, such "intermediate wetting" regimes are generally associated with strong hysteresis, which would also modify the geometry of the droplets, and dramatically complicate the pattern evolution. (In particular, we expect a breakdown of the circular symmetry of the droplets.) If the accommodation coefficient of the "dry" surface is small compared to unity (the accommodation coefficient of pure water, by definition), condensation occurs only on droplets, and the same power laws as for the 1D case are recovered,

$$\begin{gathered} \rho_i - \rho_{i,0} \sim t - t_0 \ , \\ n_i^{1/3} - n_{i,0}^{1/3} \sim t - t_0 \ . \end{gathered} \tag{6}$$

If the accommodation coefficient of the surface is not negligibly small, condensation can occur both on the droplets and on the "bare" surface (Fig. 1). Since, by definition, no accumulation of water between droplets occurs in regime (ii), droplet i collects all the water condensed on its "surface of influence" $A_{\text{inf},i}$, surrounded by the lines of zero-water-density gradient on the surface. Lacking a precise knowledge of the molecular condensation, transport process, and the droplet pattern, we will use a mean-field description of the surface of influence. Between two coalescences involving droplet i, the number of neighboring droplets does not change, and we can reasonably assume that

$$A_{\text{inf},i} \simeq \pi[\bar{a}^2(t_0) - \rho_i^2(t)] \ . \tag{7}$$

Here $2\bar{a}(t_0)$ is the average distance between droplets (Fig. 1) at time t_0. It is convenient to define a mean surface coverage

$$\epsilon^2(t) = \left[\frac{\bar{\rho}(t)}{\bar{a}(t)} \right]^2 , \tag{8}$$

so that Eq. (7) can be rewritten,

$$A_{\text{inf},i} \simeq \frac{\pi\bar{\rho}^2(t_0)}{\epsilon^2(t_0)} - \pi\rho_i^2(t) \ . \tag{9}$$

The form of the growth law is determined by the competition between two mechanisms: (1) condensation

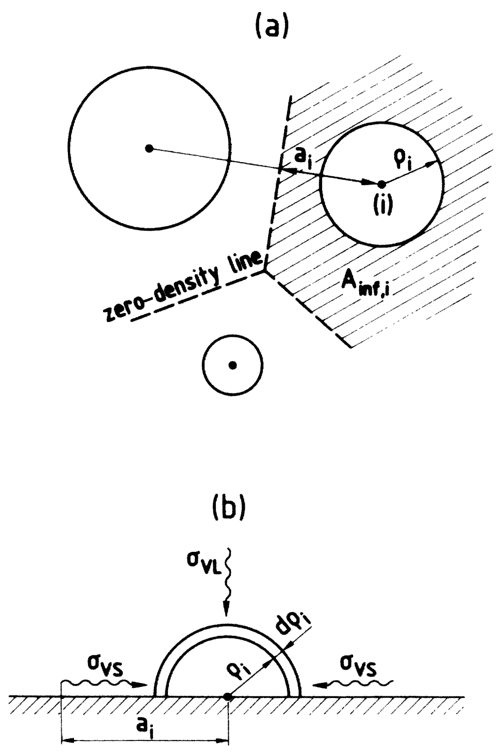

FIG. 1. Droplet condensation on a plane. (a) Top view; (b) side view, showing two competing mechanisms: condensation at the surface of the drop (accommodation coefficient σ_{VL}) and nucleation followed by diffusion of embryos at the surface between drops (accommodation coefficient σ_{VS}).

directly at the surface of the liquid droplets, and (2) nucleation of liquid embryos on the surface of influence, which diffuse to the perimeter of the droplets. There are two distinct accommodation coefficients σ_{VL} and σ_{VS} corresponding, respectively, to these phenomena.

The growth law [Eq. (2)] for droplet i can thus be estimated as

$$\frac{d\rho_i}{dt}=\frac{V_W \varphi_V A_{\mathrm{eff},i}}{2\pi\rho_i^2(t)} , \tag{10}$$

where $A_{\mathrm{eff},i}$ is given by

$$A_{\mathrm{eff},i}=\pi(2\sigma_{VL}-\sigma_{VS})\rho_i^2(t)+\frac{\pi[\bar{\rho}(t_0)]^2}{\epsilon^2(t_0)}\sigma_{VS} . \tag{11}$$

As noted above, we have assumed a constant temperature. If there were significant temperature gradients across the drop, the effective area for condensation would have been less than $2\pi\sigma_{VL}\rho^2$, corresponding to an effective accommodation coefficient smaller than that for the isothermal case.

In general, relation (10) does not lead to a simple power law. A power law for the growth is recovered when condensation on the droplet is negligible, i.e., for a low droplet coverage, $\sigma_{VS}/\epsilon^2 \gg 1$. Then,

$$n_i - n_{i,0} \sim t - t_0 , \tag{12a}$$

or

$$\rho_i^3-\rho_{i,0}^3 \sim t - t_0 . \tag{12b}$$

III. COALESCENCE

When the surfaces of two droplets i and j touch (which occurs on the contact line with the substrate for $\theta \le \pi/2$), a new drop containing n_i+n_j moles of water is formed in a fraction of a second. For weak hysteresis, the contact angle does not vary appreciably, and the new drop has a radius

$$\rho'=(\rho_i^3+\rho_j^3)^{1/3} . \tag{13}$$

If all dissipative phenomena can be neglected, the position of the center of the new droplet, $\mathbf{R}'$, is imposed by momentum conservation,

$$\mathbf{R}'=\frac{(\mathbf{R}_i\rho_i^3+\mathbf{R}_j\rho_j^3)}{(\rho_i^3+\rho_j^3)} \tag{14}$$

or, in a dimensionless representation,

$$(\mathbf{R}'-\mathbf{R}_i)=\psi_I(\nu)(\mathbf{R}_j-\mathbf{R}_i) , \tag{15}$$

where

$$\psi_I(\nu)=\frac{(1-\nu)^3}{[\nu^3+(1-\nu)^3]},\quad \nu=\frac{\rho_i}{(\rho_i+\rho_j)} . \tag{16}$$

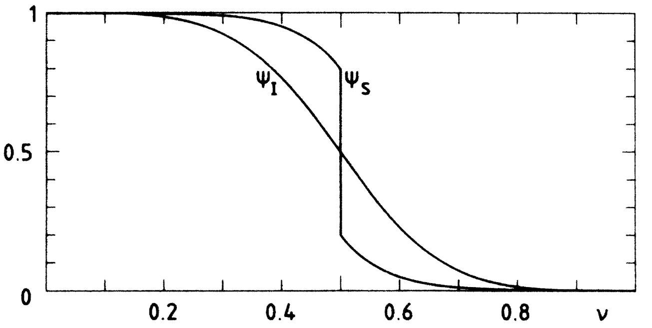

FIG. 2. Coalescence of two droplets: ψ_S, maximizing the overlap between the drops, and ψ_I, assuming momentum conservation (see text).

In actual cases, the dynamics of coalescence is driven by a balance between Laplace, viscosity, and adhesion forces, and the solution of the corresponding Navier-Stokes equations may require extensive numerical work. The situation is simpler, however, in the opposite limiting case in which dissipation dominates. In this case, it can be shown that dissipation mainly occurs in the vicinity of the triple line,[6] and the displacement can be accurately estimated by minimizing the area swept by these lines, or equivalently by maximizing the overlap between the surface contacts of the two "old" droplets and of the "new" droplet. This purely geometrical condition leads to a more complicated, but still scale-invariant, relative displacement,

$$(\mathbf{R}'-\mathbf{R}_i)=\psi_S(\nu)(\mathbf{R}_j-\mathbf{R}_i) . \tag{17}$$

The displacement ψ_S has been evaluated numerically and is compared with ψ_I in Fig. 2. The difference between ψ_S and ψ_I is significant, and it could be a very critical test of surface interactions.

IV. PATTERN EVOLUTION

If the law for the evolution of individual droplets is known, some features of the evolution of an assembly of many droplets can be predicted. Let us consider a particular realization,

$$\{\mathbf{R}_i,\rho_i\} \quad (t=0) ,$$

and another homomorphic one,

$$\{\lambda\mathbf{R}_i,\lambda\rho_i\} \quad (t=0) .$$

From relations (10) and (11), it is clear that the renormalization

$$\begin{aligned} R_i &\to \lambda R_i ,\\ A_{\mathrm{eff},i} &\to \lambda^2 A_{\mathrm{eff},i} ,\\ \rho_i &\to \lambda\rho_i ,\\ t &\to \lambda t , \end{aligned} \tag{18}$$

leaves unchanged the evolution equation for growth by condensation, as well as the equation for the occurrence of the first coalescence involving droplet i,

$$\min_j \{ |\mathbf{R}_i-\mathbf{R}_j| - [\rho_i(t)+\rho_j(t)]\} = 0 . \tag{19}$$

Equations (15) and (17) for coalescence are also invariant upon the renormalization (18), so the evolution of the entire pattern is invariant for these two limiting coalescence cases. Individual realizations of the system associated with given flow and substrate conditions can therefore be separated into homomorphic time-dependent series of patterns,

$$\{\lambda R_i, \lambda \rho_i, \lambda (t-t_0)\} \ . \tag{20}$$

It should be noticed, however, that this would not be true for more complicated, scale-dependent coalescence or growth laws. For example, scaling will not be obtained if σ is a function of ρ.

If we assume that the pattern of nucleation sites on the substrate is random and "fine grained" [i.e., smaller than the mean distance between droplets at the beginning of the growth phase (ii)], then the range of correlation is of the order of the droplet size, and all realizations are statistically independent in the "large system limit." In other words, the pattern of a realization at time t_2 can always be considered as homomorphic with a subdomain of a statistically equivalent realization at any given time t_1 [in regime (ii)]. This ensures self-similarity of the pattern. Note that this self-similarity is the direct consequence of the scale invariance of the growth processes involving one droplet.

This property, which will be very useful in Sec. V, does not, however, provide any information about the value of statistical parameters such as the polydispersity or surface coverage. These parameters are controlled by the correlated evolution of the two random distributions of sizes and positions, respectively. Information, even crude, seems difficult to obtain by means other than experiment or simulation.

V. SCALING LAWS FOR INTERMITTENT GROWTH

In this section we use a mean-field approach in the sense that all variables are spatially averaged and follow the growth of the radius $\bar{\rho}$ and content $\bar{n}$ of an average droplet. In the same manner, the number of droplets which combine during one coalescence (mostly two, but sometimes three or four on a planar substrate) is averaged as P, so that the number of droplets decreases as P^{-j}, where j is the number of coalescences.

The evolution of a typical droplet is represented schematically in Fig. 3(a). There is an alternation between continuous condensation growth (arbitrary curved lines) and coalescence (discontinuous on the scale of the experiments that have been performed and in the present theory). We call $\bar{n}_j$ and $\bar{n}_j'$ the droplet content immediately before and immediately after coalescence j, respectively; $\bar{\rho}_j$ and $\bar{\rho}'_j$ are the corresponding radii. Let us consider the time interval $(t_{j+1}-t_j)$, between coalescences j and $j+1$. In the two limiting cases of $\sigma_{VS} \simeq 0$ and $\sigma_{VS}/\epsilon^2 \gg 1$ (dominant droplet capture and dominant substrate capture, respectively), there is a power-law relation between the elapsed time, the droplet size, and the droplet size at the end of the latest coalescence [Eqs. (6) and (12)]. A scaling treatment is rigorously justified (within the mean-field approximation). Since σ is at most unity, intermediate cases [Eqs. (10) and (11)] therefore correspond to high ϵ^2 values, and the relative growth of one droplet between two coalescences is relatively weak. Thus, even in these cases, a good scaling description can be obtained by assuming the approximate "local" power law,

$$\frac{d\bar{n}(t)}{dt} \simeq [\bar{\rho}(t)]^{\delta_c-\beta}[\bar{\rho}_j(t_j)]^{\beta}\varphi_V \ . \tag{21}$$

This growth law derives from Eqs. (10) and (11). The exponent δ_c is the dimensionality of the space in which condensation occurs (most generally a surface, so $\delta_c=2$, but generalization to fractals is possible). The exponent β can vary between 0 and 2; $\beta=0$ corresponds to condensation on droplets only [$\sigma_{VS}=0$ in Eq. (11)], and $\beta=2$ corresponds to an equivalent condensation on both the droplet and its influence area [$\sigma_{VS}=\sigma_{VL}$ in Eq. (11)]. After integration, Eq. (21) becomes

$$\bar{n}^{\delta}-\bar{n}_j'^{\delta} \simeq \bar{\rho}_j'^{\beta}(t-t_j) \ , \tag{22}$$

where $\delta=(\delta_d-\delta_c+\beta)/\delta_d$, with δ_d the dimensionality of

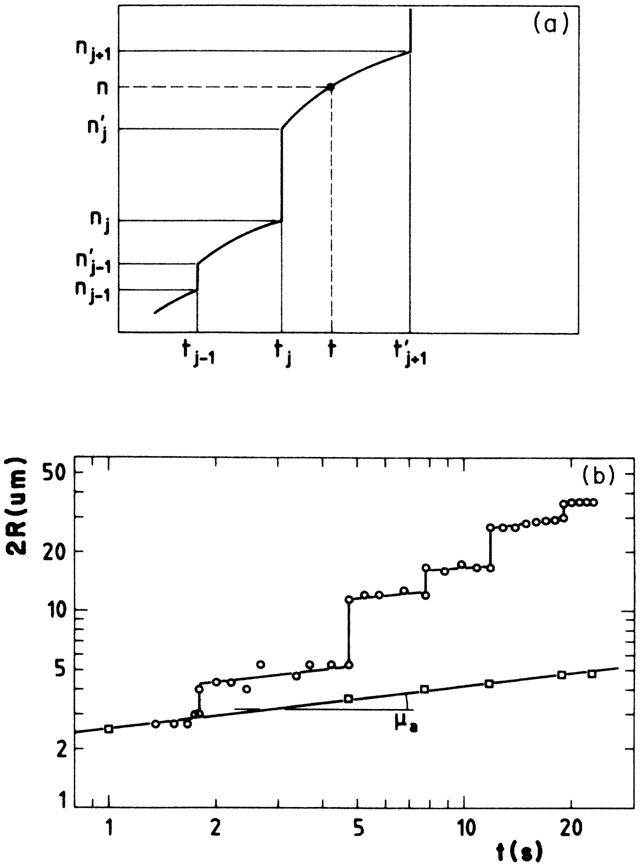

FIG. 3. (a) Evolution of a typical or "mean-field" droplet. (b) Experimental evolution of a typical droplet (log-log plot, from Ref. 4). The squares represent the time evolution after removing the effect of coalescences.

the droplet. In the experimental situation of Ref. 4, $\delta_d=3$, but 2D or even fractal objects may be relevant to other situations.[7]

The recursion relation is readily derived from (22) as

$$\frac{\bar n_{j+1}^{\delta}-\bar n_j'^{\delta}}{\bar n_j^{\delta}-\bar n_{j-1}'^{\delta}}=\frac{t_{j+1}-t_j}{t_j-t_{j-1}}\left[\frac{\bar n_j'}{\bar n_{j-1}'}\right]^{\beta/\delta_d} . \quad (23)$$

For large j, straightforward algebra leads to the scaling relation,

$$\bar\rho_j \sim t_j^{\mu_0} , \quad (24)$$

with

$$\mu_0=1/(\delta_d-\delta_c) . \quad (25)$$

According to this relation, the overall growth rate should depend on the difference in dimensionality between the droplets and the substrate, but should not depend on the time exponent of the growth of an individual droplet, provided the renormalization of A_{eff} expressed in relations (18) is not affected. Indeed, the growth-rate exponent μ_0 can be derived directly by using macroscopic mass conservation laws, and ignoring the details of the growth mechanism.[8] Self-similarity in growth has to be assumed, however, in this approach.

Finally, it is interesting to discuss the "apparent single-droplet exponent," as evaluated by Beysens and Knobler.[4] In this procedure [pictured in Fig. 3(b)], the apparent droplet size $\tilde\rho$ is renormalized after each coalescence to its size just before this coalescence. This amounts to defining an equivalent system in which no coalescence occurs, i.e., in which the number of droplets remains constant, but whose average water surface density $\bar D$ corresponds to that of the real system. $\bar D$, in the equivalent system, scales as

$$\bar D \sim (\tilde\rho)^{\delta_d} \sim t^{\mu_a\delta_d} \quad (26)$$

by definition, whereas the surface density of the actual system scales as

$$\bar D \sim N\bar\rho^{\,\delta_d} . \quad (27)$$

The scaling behavior of the number density of droplets, N, is obtained using the self-similarity of the actual system in dimensionality δ_c,

$$N \sim \bar\rho^{\,-\delta_c} , \quad (28)$$

allowing the relation between μ_a and μ_0 to be obtained:

$$\mu_a=\mu_0(\delta_d-\delta_c)/\delta_d . \quad (29)$$

Note that the growth of hemispherical droplets on a planar surface always leads to $\mu_0=1$, $\mu_a=\frac{1}{3}$, whereas the actual exponents for the growth of an individual droplet are $\frac{1}{3}$ for a surface-dominant condensation and 1 for droplet-dominant condensation, respectively.

Our predictions are significantly different from the experimental observations ($\mu_0=0.75$ and $\mu_a=0.23$). Since the exponent $\mu_0=1$ is merely a consequence of self-similarity, constant condensation flux, and mass conservation, we can see only two possible explanations for this discrepancy.

(a) Our assumption of a constant net incoming flux of water molecules on the surface is oversimplified. In particular, the evolution of the droplet size changes the roughness of the surface. In some hydrodynamic conditions, this may lead to boundary-layer effects and to an effective φ_V, decreasing with increasing droplet size (or, equivalently, a generalized effective surface A_{eff} with a radius exponent smaller than 2).

(b) The assumption that the water impinging on the surface is entirely collected by the visible droplets in regime (ii) is also disputable. Since other visible droplets appear between the old ones in regime (iii), this assumption must break down somewhere.

One can modify the scaling description by allowing the radius exponent for A_{eff} to vary. This can be accomplished by replacing Eq. (21) by

$$\frac{d\bar n(t)}{dt} \simeq [\bar\rho(t)]^{\delta_c-\beta}[\bar\rho_j(t_j)]^{\beta}\left[\frac{\bar\rho(t)}{\rho}\right]^{-\alpha}\varphi_V , \quad (30)$$

where ρ is a characteristic length and α an exponent with a value between 0 and δ_c. As a result, μ_0 is modified,

$$\mu_0'=1/(\delta_d-\delta_c+\alpha) , \quad (31)$$

but Eq. (29) remains unchanged and, for breath figures, the mean droplet radius exponent remains equal to $3\mu_a$. Values of the phenomenological exponent α in the range 0.3–0.4 would reconcile the theory with the experiments described in Ref. 4, but further experiments and, in particular, condensation experiments performed in well-defined hydrodynamic conditions are necessary to clarify the underlying physics.

VI. CONCLUDING REMARKS

Several essential aspects of the condensation processes have been deliberately ignored in the present development of scaling arguments. The first one is the hydrodynamic aspect. Very delicate questions may be raised by the hydrodynamics of the incipient gas, turbulence, and boundary-layer problems. Most importantly, is there any difference between a flow of pure water vapor and a flow of a gas, e.g., nitrogen, as in Ref. 4, saturated with water? It would be interesting to perform experiments under flux conditions that are as well defined as possible, in order to allow a more critical comparison to be made between theory and experiment. Another difficulty arises with the more microscopic question of the hydrodynamics of the coalescence process itself. Fortunately, the behavior probably affects only the details of the distribution of positions. Polydispersity may be affected to some extent, but not the growth rates. As noted previously, the mean-field nature of the theory provides no access to polydispersity aspects and fluctuations.

By limiting ourselves to regime (ii), we have also avoided the problems related to the nucleation and the migration of water on surfaces. Nucleation has been studied rather thoroughly, and other experimental situations are probably more suitable for studying it in detail. But we believe that the growth of breath figures raises very original and interesting questions in relation to the migration of nucleated aggregates on a substrate.[7] Some developments along these lines will be proposed in the near future.

Note added in proof. Recent computer simulations [C. D. Fritter and C. M. Knobler (unpublished)] have demonstrated the validity of Eq. (29) for the growth of two- and three-dimensional droplets on a one-dimensional surface.

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