Scaling in the growth of aggregates on a surface

D. Beysens

*Service de Physique du Solide et de Résonance Magnétique, Département de Physique Générale,
Institut de Recherche Fondamentale du Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Saclay,
Ormes des Mérisiers, F-91191 Gif-sur-Yvette CEDEX, France*

C. M. Knobler

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024-1569

H. Schaffar

*Laboratoire des Propriétés Physiques des Couches Minces, Faculté des Sciences et des Techniques
Saint-Jérôme, Université de Droit, d'Economie et des Sciences d'Aix-Marseille III, Avenue Escadrille Normandie-Niemen,
F-13397 Marseille CEDEX 13, France*

An analysis is presented of the growth of silver aggregates in the size range 10–200 Å on an amorphous carbon substrate (a-C). It is found that growth at this submicroscopic scale exhibits the main statistical properties observed on a scale of 10^{-3}–1 mm in the patterns formed when a vapor (water) condenses on a surface that is incompletely wetted by the liquid droplets; that is, the phenomenon of "breath figures." The similarity is striking and is interpreted as a consequence of the scaling properties induced by the coalescence of domains.

I. INTRODUCTION

The condensation of vapors on solid surfaces is an essential part of a number of processes of technical importance, and studies of the kinetics of condensation and growth have therefore been undertaken by scientists in a variety of disciplines. Materials scientists have been led to this topic by their interest in the preparation of thin films;[1–3] engineers have studied the enhancement in heat transfer when a fluid condenses in the form of droplets rather than as a film.[4] There have been recent investigations of a closely related phenomenon, breath figures (BF), the patterns formed when droplets of water condense and grow on glass surfaces.[5]

A sizeable amount of literature has developed independently in each of these areas, but the workers in one field have generally not been aware of the efforts in another. We have discovered that the evolution of the pattern of droplets when water condenses on glass is quantitatively similar to that observed when vapors of metals such as silver condense on solids. There is a remarkable congruence between these processes, although they take place on length scales that differ by 5 orders of magnitude.

This relationship, which will be demonstrated in this paper, follows from scaling arguments that can be applied irrespective of the underlying growth mechanisms. The scaling relations are implicit in similarity solution description of island growth, such as that employed by Vincent,[6] but they have not been fully exploited. As we will show, relatively simple experiments made on a micron to millimeter scale can provide insights about phenomena on a 20–200 Å scale that are difficult to measure.

II. GROWTH OF BREATH FIGURES

Three successive stages of growth can be identified.

(i) Droplets nucleate and grow with no significant interactions (coalescence) between them. The droplets that are visible do not move during their growth. The average droplet radius $\langle R \rangle$ increases according to a power law

$$\langle R \rangle \propto \tau^x , \tag{1}$$

where τ, the scaled time, is the product of the time t and the square root of the volumetric flow rate F: $\tau \rightarrow t\sqrt{F}$.[7] The exponent x has been found to be $\frac{1}{4}$ in some experiments[5] and $\frac{1}{3}$ in others.[8] A reexamination[7] of the conditions of the experiments leads to the conclusion that the lower exponent is the result of temperature gradients in the substrate, and that $\frac{1}{3}$ is consistent with all of the studies.

(ii) When the surface coverage ϵ^2 becomes sufficiently large, the droplets interact by coalescence, which makes them move. The coalescences limit the size of droplets and continuously rescale the pattern. In this regime there is a single natural length scale $\langle R \rangle$, and all spatial characteristics of the pattern scale with it. The pattern is self-similar and the statistical properties of the ensemble of droplets (correlation function, distribution of radii, polydispersity) become time invariant. The surface coverage remains constant at a value of 0.55, which is very close to the "jamming limit," the limit of packing in the process of random sequential adsorption in two dimensions.[9]

The average radius continues to follow a power law but with an exponent $y = 3x$. It can be shown quite generally[10] that y and x are related by the dimensionality of the

condensing droplets D_d and that of the surface on which they condense, D_s: $y = [D_d/(D_d - D_s)]x$.

(iii) At a time at which the actual (unscaled) distance between droplets reaches a critical value, small droplets begin to be apparent between the large droplets. This new generation of droplets grows in turn through each of the stages. Thus, after some time a number of different generations can be found on the surface, each of which corresponds to a particular period of growth and each of which can exhibit the self-similarity properties typical of stage (ii).

It is also possible for the regularity of the patterns to be limited by hysteresis in the contact angle. In the case of such a nonuniform surface, two droplets that are sections of a sphere (hemispherical in the case of water on silanized glass surfaces) may coalesce into a droplet that has the form of an ellipsoid. This imperfection affects the surface coverage and may lead to an irregular, pseudowetting film.

The scaling behavior and the way in which the collective properties of breath figures arise from coalescences has been examined theoretically[10] and by computer simulation.[11] It is assumed in these treatments that individual droplets grow according to a power law. The details of the mechanism that leads to this power law are less well understood.

III. VAPOR DEPOSITION OF METALS

It is well established[1-3] that under certain circumstances the vapor deposition of metals leads to solid aggregates that can coalesce to form larger aggregates with the same form. In addition, when the temperature of the substrate is not too high (e.g., room temperature),

their Brownian motion is negligible. Such aggregates then behave like liquid droplets.

The morphology of the aggregates, the number density, and the size distribution can be determined by electron microscopy. The evolution of the droplet patterns is determined by comparing samples that have been prepared at a constant deposition rate for different periods of time. An equivalent measure of the time is the average film thickness d, a quantity that is often reported.

When granular metallic films are exposed to air they may undergo irreversible changes in morphology. The films can be stabilized, however, by covering them with an amorphous carbon or SiO overlayer before the vacuum chamber in which they are prepared is vented. Electrical conductivity measurements[12,13] show that this procedure introduces some coalescences but alters the film only slightly.

IV. COMPARISON BETWEEN BREATH FIGURES AND METALLIC AGGREGATES

To demonstrate the relation between the growth of BF and the growth of metallic aggregates, we analyze measurements of the vapor deposition of silver on amorphous carbon (a-C). There are many results reported in literature [see, e.g., the review (Refs. 1–3)]; we have chosen to analyze a recent study by one of us (H.S.).[13]

Electron micrographs of a layer deposited on a (a-C) bent substrate allow the aggregates to be seen edge on and show that they resemble liquid droplets that do not wet the surface (Fig. 1). The droplets are slightly ellipsoidal in shape. Distorted droplets may also be observed in BF and arise when there is considerable hysteresis in

FIG. 1. Electron micrographs of Ag aggregates on a bent substrate of amorphous carbon (a-C). $T = 20\,°C$, deposition rate $= 0.1$ pm s^{-1}.
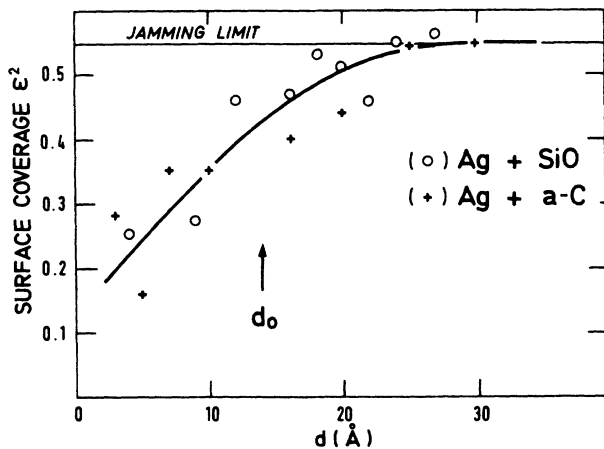
FIG. 2. Fraction of surface covered by the aggregates during this growth. The thickness d has the significance of a reduced time (see text). At d_0 the interactions between aggregates become important. The experiments have been conducted at $T=20\,°C$, with a deposition rate of 0.1 pm s^{-1}. Details can be found in Ref. 13.

the contact angle. The nonspherical shapes of the silver aggregates are not attributable to the same cause but the effect on the droplet pattern evolution is the same.

The evolution of the size distribution $n(R)$ of the aggregates can be determined from an analysis of electron micrographs of deposits made at different stages of growth, i.e., at different values of d. Since some of the droplets are ellipsoidal, R is taken as the largest dimension.

Three important quantities can be obtained from $n(R)$: (1) the surface coverage ϵ^2, Fig. 2; (2) the average radius $\langle R \rangle$, Fig. 3; and (Fig. 4) the size distribution rescaled by $\langle R \rangle$, $n^*=N(R/\langle R \rangle)/n_{max}$, where n_{max} is the maximum in a smooth distribution drawn through the histograms. In some cases the distribution is bimodal; a small secondary maximum is found at small sizes. These subsidiary peaks have not been considered in the analysis.
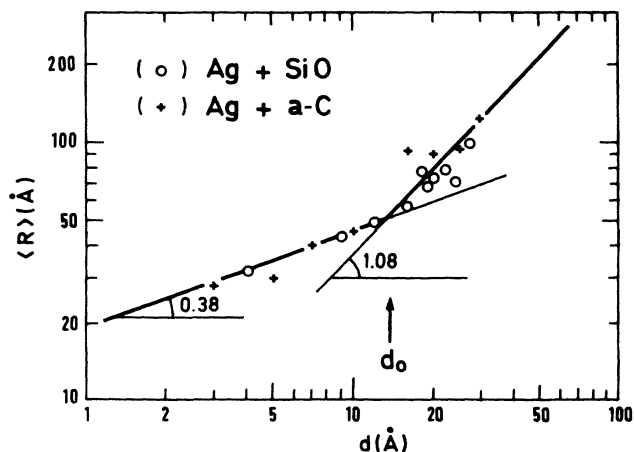

FIG. 3. Behavior of the average size $\langle R \rangle$ of the aggregates.

The behavior of the quantities ϵ^2, $\langle R \rangle$, and n^* seen in the figures is strikingly similar to that observed for BF. It is evident from Fig. 3 that there are two distinct growth regimes. At early times the growth of the average radius can be represented by a power law with an exponent $x=0.38$, in relatively good agreement with the value $\frac{1}{3}$ found for water-droplet growth. At a "time" $d_0=13$ Å there is a sharp transition to more rapid
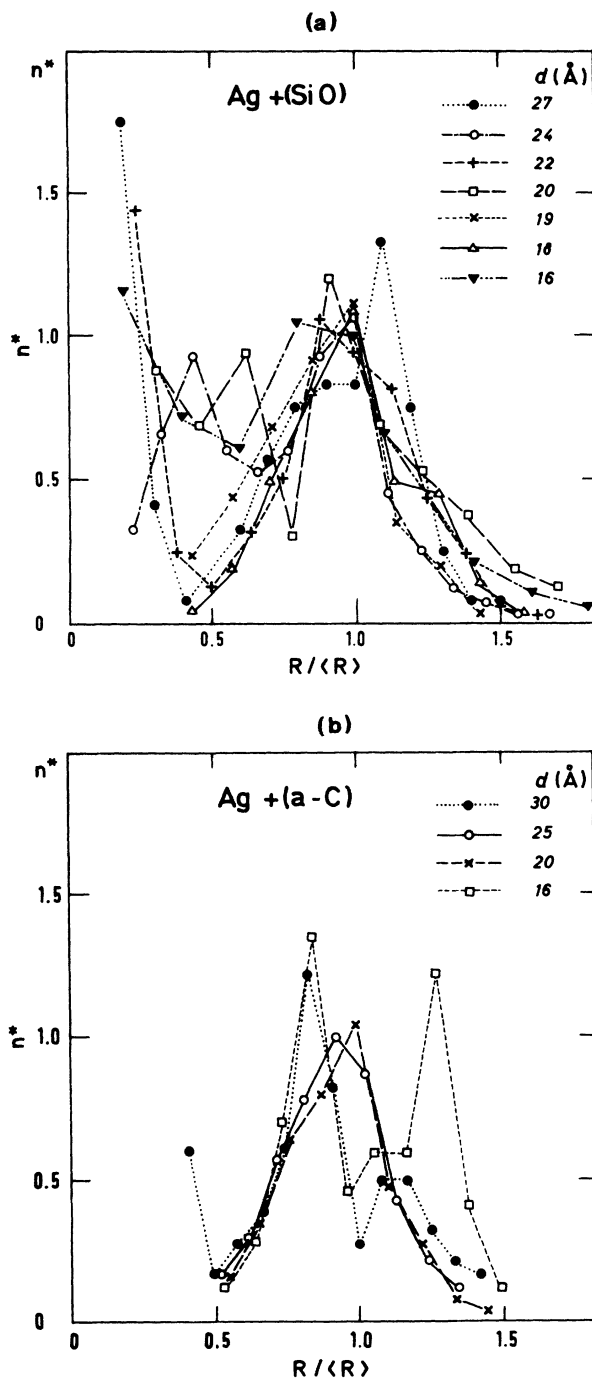

FIG. 4. Scaled aggregate size distribution (see text) of (a) pattern stabilized by deposition of SiO, (b) pattern stabilized by deposition of a-C.
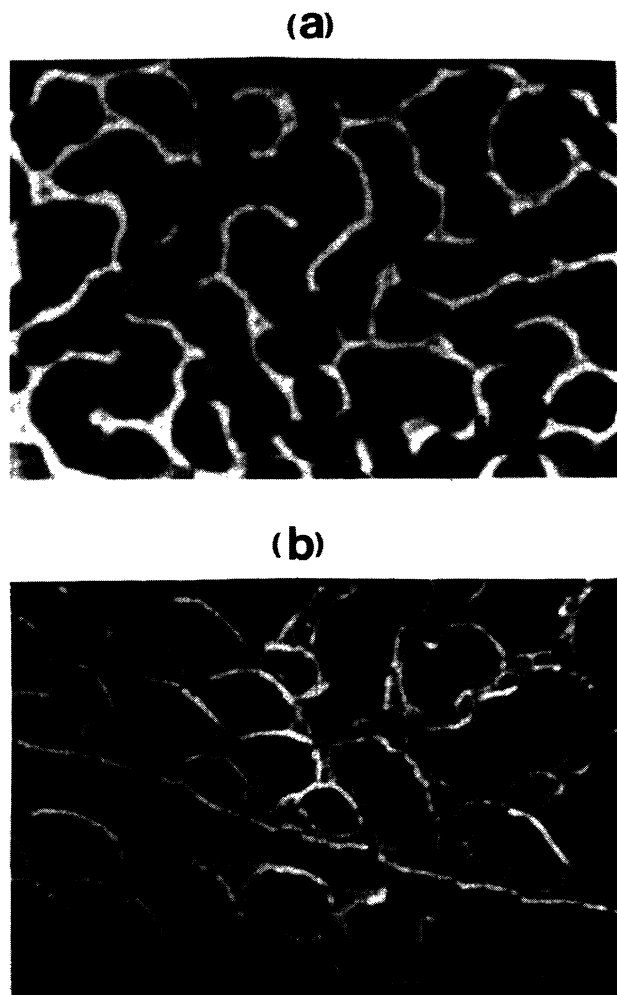
(a)

(b)

FIG. 5. (a) Stage of growth where the aggregates no longer behave like liquid droplets on a homogeneous surface. (b) Comparison with the same stage of growth for liquid droplets (BF) with hysteresis of the contact angle.

growth, which can be described by a power law with an exponent $y = 1.08$. Thus, as in BF, the relation $y = 3x$ holds.

As in BF, the coverage rises during the first stage of growth and then levels off at the jamming limit when coalescence begins to become important. This leveling can be made less visible than for BF because of the anisotropy in coalescence (see below). Constant coverage is a hallmark of the self-similar regime. Another characteristic of self-similarity, the scaling of the size distribution, is seen in Fig. 4. The presence of a secondary maximum may be interpreted, as in BF, as the appearance of a new generation on the surface that has been cleared by coalescence.

The self-similar regime in these experiments is markedly shorter than that observed in BF. It is likely that large solid particles are less liquidlike than small ones in that they cannot rearrange into compact aggregates after coalescences. The anisotropy of the aggregates therefore increases with their size, causing the coverage to exceed the jamming limit. A percolation threshold is reached [Fig. 5(a)], and a thick film is finally formed. A similar transformation is seen in BF when there is strong hysteresis in the contact angle [Fig. 5(b)].

It is striking that Ag aggregates in the size range 10–200 Å are formed and grow in much the same way as water droplets with sizes from 0.001–1 mm. Many other examples of the formation of granular films are known,[14] and where appropriate growth data are reported, there is clear evidence of the correspondence with BF. For example, the measurements by Ozawa and Fujiwara[15] on the growth of bismuth aggregates on carbon show single-particle $(t^{1/3})$ growth at 125 °C, while studies at 30 °C on SiO give evidence of the start of the crossover to coalescence-dominated (t) growth.

We have not addressed the mechanisms of growth of individual droplets. These are obviously of importance if we are able to have a full understanding of film growth, and have been analyzed in refined theories.[2,3] Such mechanisms are also important for aspects other than thin-film technology; the strength of the scaling analysis is, however, that it does not depend on the detailed mechanisms (provided that they preserve scale invariance, as is the case for power-law growth). Scaling of the pattern is a consequence only of the coalescence phenomenon, which is at the origin of the similarity between BF and thin solid film growth—and which also fixes its limits. Coalescence also induces correlation between the growing aggregates, as seen in the simulations.[11] Though the data of Zaughi et al.[16] on gold nuclei on a KCl substrate have not been obtained under the same conditions that apply to the experiments that have been analyzed here, it would be very interesting to compare the shape of the radial distribution of nuclei with that which develops as the result of coalescence. (In Ref. 16 the radial distribution was interpreted as coming only from repulsive forces between nuclei.) This correlation also may account for the failure of Vincent's similarity solution[6] to give the correct relation between the growth law for the radius of a single droplet and that for the average radius.

ACKNOWLEDGMENTS

[1]See, e.g., *Nucleation and Growth of Thin Films*, edited by B. Lewis and J. C. Anderson (Academic, London, 1978), and references therein.

[2]J. A. Venables, G. D. T. Spiller, and M. Handbücken, Rep. Prog. Phys. **47**, 399 (1984).

[3]A. D. Gates and J. L. Robins, Thin Solid Films **149**, 113 (1987).

[4]See, e.g., J. W. Rose and L. R. Glicksman, Int. J. Heat Mass Transfer **16**, 411 (1973), and references therein.

[5]D. Beysens, D. Fritter, D. Roux, C. M. Knobler, and J. L. Viovy, in *Dynamics of Ordering Processes in Condensed Matter,* edited by S. Komura and K. Kawasaki (Plenum, New York, 1988), and references therein.

[6]R. Vincent, Proc. R. Soc. London, Ser. A **321**, 53 (1971).

[7]D. Fritter, Ph.D. thesis, Department of Chemistry, UCLA, 1989.

[8]C. M. Knobler and D. Beysens, Europhys. Lett. **6**, 707 (1988).

[9]E. L. Hinrichsen, J. Feder, and T. Jossang, J. Stat. Phys. **44**, 793 (1986), and references therein.

[10]J. L. Viovy, D. Beysens, and C. M. Knobler, Phys. Rev. A **37**, 4965 (1988).

[11]D. Fritter, C. M. Knobler, D. Roux, and D. Beysens, J. Stat. Phys. **52**, 1447 (1988).

[12]G. Desrousseaux, J. Trompette, R. Faure, H. Schaffer, and J. P. Dussaulcy, Thin Solid Films **98**, 139 (1982).

[13]G. Desrousseaux, A. Carlan, B. Robrieux, H. Schaffar, J. Trompette, J. P. Dussaulcy, and R. Faure, J. Phys. Chem. Solids **46**, 929 (1985); H. Schaffar, Ph.D. thesis, Faculté des Sciences et des Techniques Saint-Jérôme, Université de Droit, d'Economie et des Sciences d'Aix-Marseille III, 1987).

[14]See, e.g., S. Stoyanov and D. Kaschiev, in *Current Topics in Materials Science,* edited by E. Kaldis (North-Holland, Amsterdam, 1981), Vol. 7, p. 69.

[15]S. Ozawa and S. Fujiwara, Thin Solid Films **37**, 73 (1976).

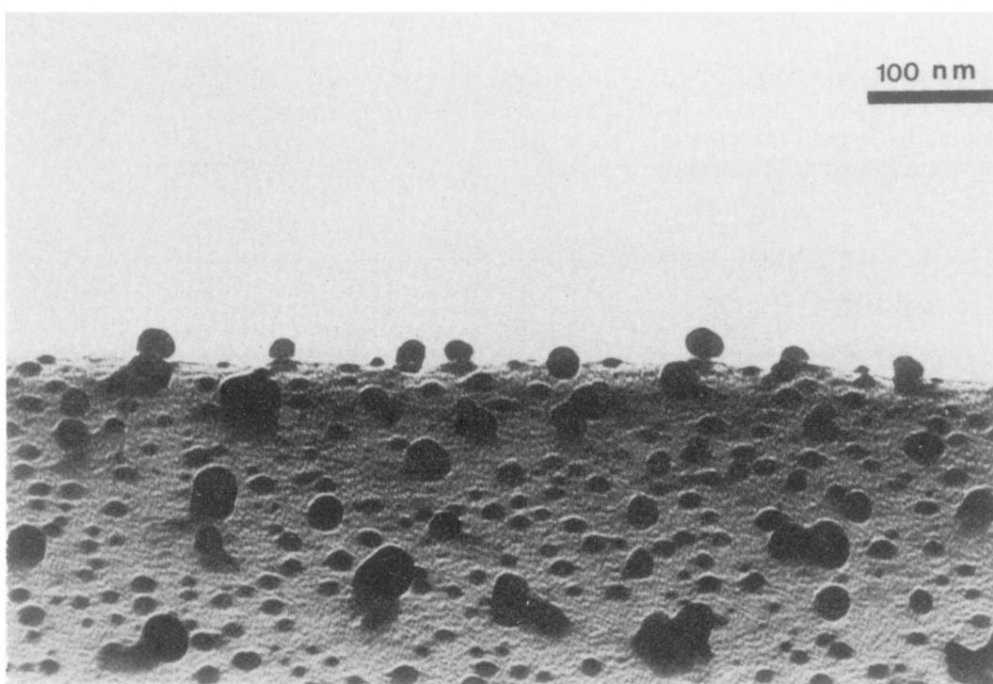[16]J. C. Zaughi, J. J. Metois, and R. Kern, Surf. Sci. **52**, 556 (1975); J. J. Metois (private communication).

FIG. 1. Electron micrographs of Ag aggregates on a bent substrate of amorphous carbon (*a*-C). $T = 20\,°C$, deposition rate $= 0.1$ pm s^{-1}.
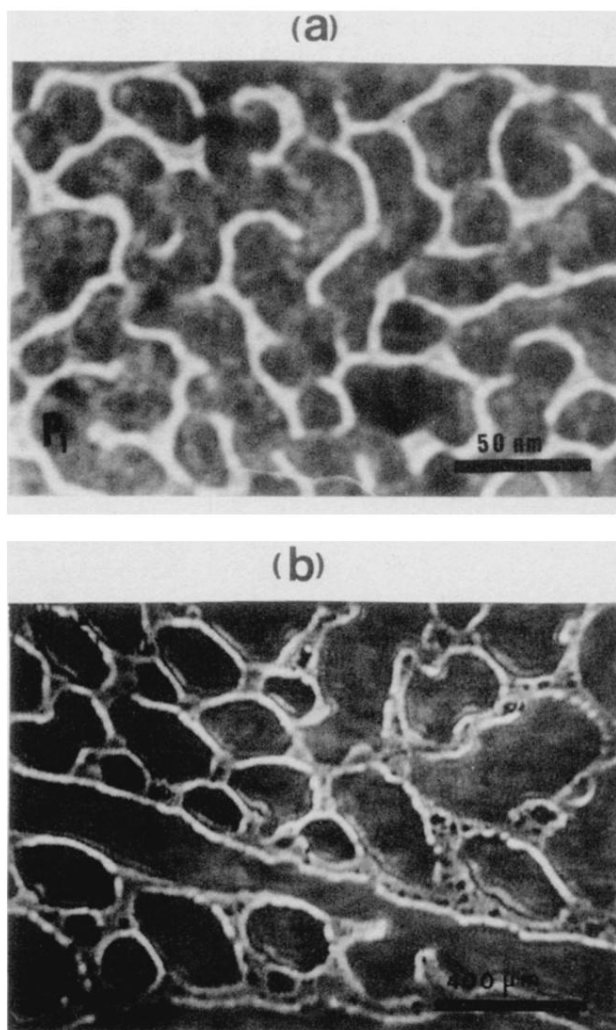
FIG. 5. (a) Stage of growth where the aggregates no longer behave like liquid droplets on a homogeneous surface. (b) Comparison with the same stage of growth for liquid droplets (BF) with hysteresis of the contact angle.