Two-dimensional ordering during droplet growth on a liquid surface

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In contrast to the breath-figure patterns that arise when water condenses on solid surfaces, the condensation and growth of droplets of water on paraffin oil can produce distinct two-dimensional structures. These occur because, in contrast to droplets on a solid surface, droplets of an immiscible fluid on the surface of a liquid can interact by mechanisms other than coalescence. An experimental investigation of the translational and orientational order in the patterns enables a connection to be made between their morphology and growth.

I. INTRODUCTION

The morphology of growing domains can provide clues to the nature of the processes by which they grow. We present here a study of the relation between the growth and the structure of the patterns of droplets that form when water condenses on the surface of paraffin oil, a liquid in which it is not soluble. Such two-dimensional droplet condensation patterns have been called breath figures (BF), and extensive measurements of the patterns that occur when fluids condense on solid surfaces have been carried out.[1,2] We focus here on the BF that form on liquid surfaces;[2] the interactions between droplets in this case are more complex than those when the growth occurs on a solid and more complex morphologies may be expected.

Our principal finding is that an ordered droplet structure develops during growth that has the appearance of a hexagonal two-dimensional crystal with many defects. A close analogy can be made between the growth of BF on liquids and two-dimensional solidification. In both cases the system evolves from disorder to order continuously, which suggests that a hexatic phase[3] might be an intermediate in the process.

We begin by briefly reviewing the main characteristics of the growth of BF. We will then describe the evolution of the structures and characterize them; their topology will be correlated with the different stages of growth.

II. GROWTH LAW FOR BF

The growth of BF on liquids is found[2] to evolve through several stages similar to those observed on solids and found in simulations.[4] These characteristics are delineated in Figs. 1 and 2 and described below.

(i) Initial stage. Here the droplets are isolated and do not interact strongly. The surface coverage (the fraction of the oil surface occupied by the droplets) is low and the average droplet radius $\langle R \rangle$ varies as $\langle R \rangle \propto t^{1/3}$.

(ii) Crossover stage. This stage of growth is characterized by a high surface coverage and a marked increase in the rate of droplet growth.

(iii) Coalescence-dominated stage. Here the surface coverage is high and constant. Its value is about 0.55, that found on solid substrates. In this stage, droplet coalescence markedly accelerates the growth and continuously rescales the pattern. The pattern remains self-similar and the average droplet radius grows as $\langle R \rangle \propto t$.

The differences between droplet growth on solids and liquids stem from differences in the nature of the interactions between the droplets. On a solid surface, the droplets have the form of sections of a sphere (they are essentially hemispherical on silanized glass). Macroscopic droplets move only because of coalescences. There can therefore be no rearrangement to increase the surface cov-
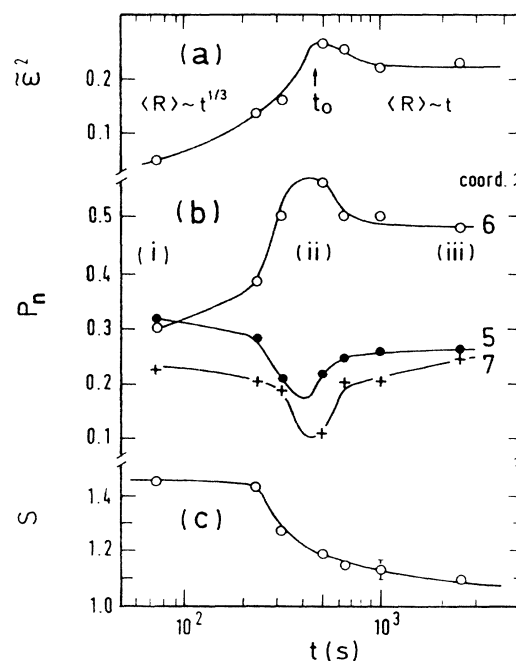

FIG. 1. Time evolution of (a) the apparent surface coverage $\tilde{\varepsilon}^2$; (b) the distribution P_n of polygons with coordination numbers $n = 5, 6, 7$; (c) the entropy S of configuration per drop.
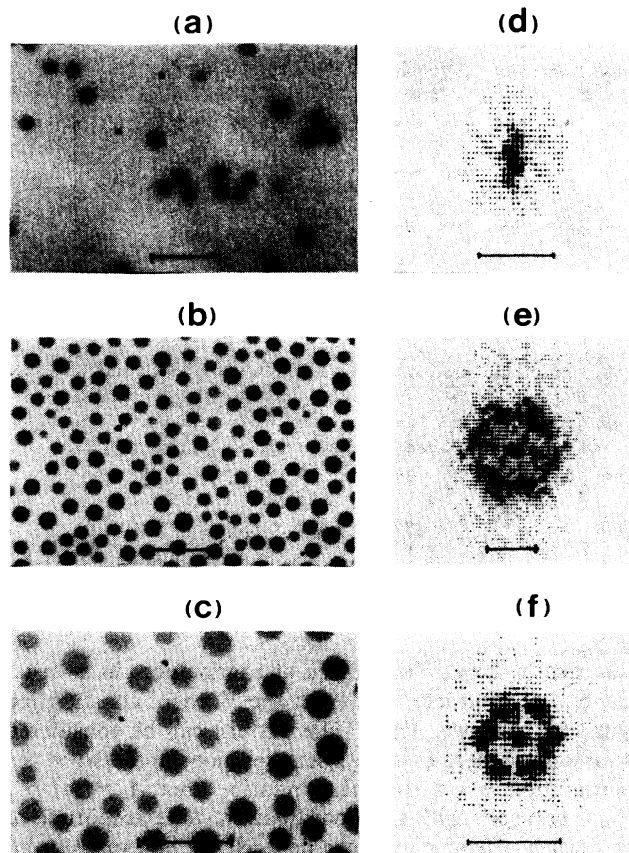
FIG. 2. Three typical stages of growth illustrated by photos in direct space (a)–(c) and the corresponding structure factor (d)–(f). (a) and (d) refer to stage (i), (b) and (e) to stage (ii), and (c) and (f) to stage (iii). The bars correspond to (a),(b), 50 μm; (c), 400 μm; (d),(e), 0.5 μm^{-1}; (f), 0.1 μm^{-1}.

erage, so the droplet pattern remains liquidlike. This can be seen in the structure factor obtained by light scattering[1] and that calculated from simulations.[4]

Droplets of water on the surface of paraffin oil have a complex shape. Water is denser than oil, but the droplets do not sink because surface tension forces counterbalance their weight. Only a small part of the droplet rises above the surface of the oil. In contrast to droplets on solid surfaces, water droplets on oil do not coalesce immediately when they touch because they are separated by a thin film of oil. Coalescence can occur only after the film has thinned,[5] a time long enough for the droplets to interact as though they were hard spheres. Coalescence generates defects in the structure but allows a reorganization of the pattern because the interactions upon coalescence can extend to droplets other than those that coalesce.

The droplet interactions are thus of two types: a long-ranged attraction due to the deformation of the substrate,[6] and a short-ranged, hard-sphere-like repulsion connected to the coalescence time delay.

III. ANALYSIS OF THE PATTERNS

We will now show that as a result of these interactions the droplet pattern evolves from a totally disordered struc-ture in stage (i) into an ordered pattern in stage (iii). The experimental procedures have been described.[2] Four experiments, performed at different temperature of condensation and vapor flow rate have been analyzed in detail. We report here only a typical experiment where the temperature of the oil was 12.2 °C, that of the saturated vapor 20.2 °C, and the flow rate 9.6 cm^{3}s^{-1}. The uniformity of the pattern was found to be highly sensitive to all sources of pollution, especially dust in the oil. Typical droplet patterns, viewed from above, are shown in Fig. 2. Note that most of a droplet lies beneath the surface, so the real diameter has to be estimated; the ratio of the apparent to real diameter is about 1:1.4.[2] As a result, one defines an apparent cross-sectional coverage $\bar{c}^2$, connected to the apparent sectional area of the drops, and which is different by the factor $(1.4)^2$ from the actual surface coverage.

A. Structure Factor

Patterns recorded on videotape were digitized by means of an image analysis system (256 intensity levels). A two-dimensional (2D) Fourier transform of the corresponding intensity was then performed. This allowed the structure factor of the pattern to be obtained. Typical structure factors corresponding to each stage of growth are shown in Fig. 2. They exhibit the following characteristics:

In stage (i) no structure is visible and the pattern has the appearance of a gas, though locally the droplets tend to arrange as clusters.

During the crossover stage (ii), a ring with a fuzzy periodic structure can be seen. The existence of a ring demonstrates that there is a characteristic interdroplet distance and the weakness of the angular dependence shows that the orientational order is poor. Direct-space observation confirms this description. Droplets are closely packed with a center-to-center separation of the order of their diameter.

In the coalescence-dominated stage (iii), a sixfold modulation appears more clearly in the structure factor, but the spots remain diffuse. The pattern can be interpreted as arising from translational order in an imperfect two-dimensional crystal that has little orientational order. In direct space one observes drops aligned along lines perpendicular to the spot direction.

The total number of drops in any one image is small and the structure factor is biased by the form factor of individual drops. It is therefore difficult to interpret the structure factor quantitatively, and for this reason we have turned to some direct-space techniques in order to characterize the order.

B. Voronoi Polygons

The Voronoi construction is a well-known method for characterizing unambiguously the correlations between neighboring points on a surface.[7] The sides of the Voronoi polygon around a droplet are the bisectors of the lines between the droplet and its neighbors (Fig. 3). In the following we investigate the level of translational and orientational orders in four different ways:
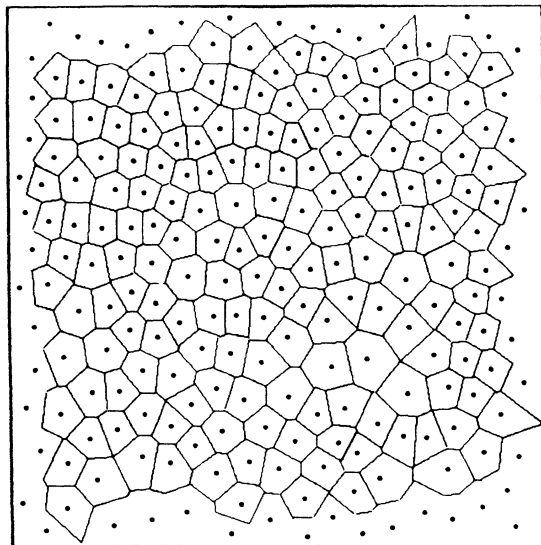
FIG. 3. Voronoi polygons from a pattern of droplets. Voronoi polygons are obtained by drawing the perpendicular bissecting lines to the lines joining any two drops. These polygons are the smallest convex polygons surrounding any given drop.

1. Coordination. The coordination number (n) of a droplet is the number of sides of its Voronoi polygon. Figure 1(b) shows for each of the stages the fraction of droplets P_n that exhibit a given coordination n. Note the change in the number of five-, six-, and seven-coordinated droplets with time. In stage (i), five- and six-coordinated droplets constitute the largest part of the population. The distribution of coordination numbers is very asymmetric, a characteristic of a gaslike system.[7] The fraction of six-coordinated droplets increases dramatically during the crossover stage, indicating a transition to a closer-packed structure, which is also seen as a hump in the surface coverage. In the last stage, sixfold coordination decreases, but the distribution becomes more symmetric, which is the
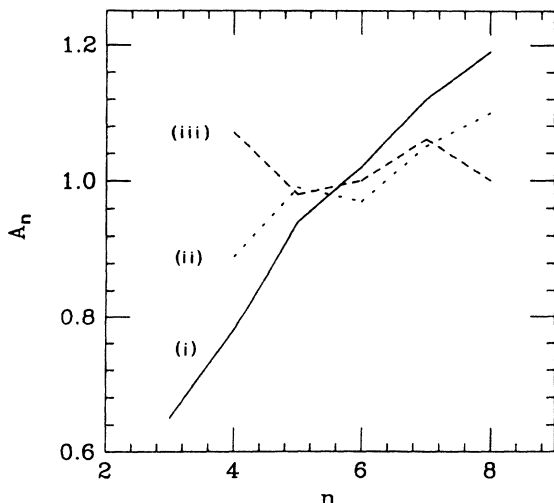

FIG. 4. Lewis' law. (A_n is normalized to the mean area of the polygons.)
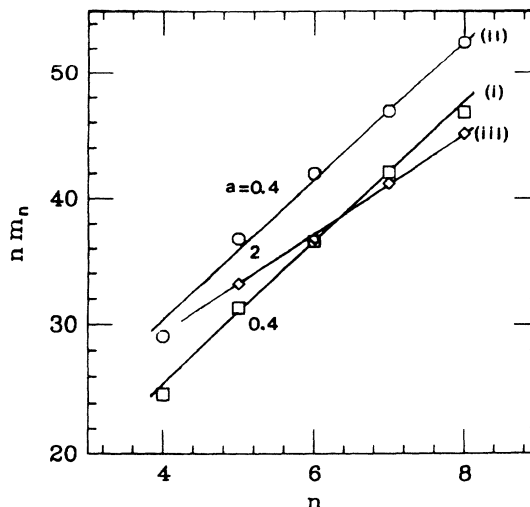

FIG. 5. Aboav's law.

signature of a hexagonal 2D crystal with many 5-7 defect pairs.

2. Lewis' Law. The degree of randomness in a structure can be characterized from the Voronoi construction by means of Lewis' law.[8] The pattern can be considered as random if there exists a linear relationship between the coordination n and the mean relative area $A_n = \langle A(n) \rangle / \langle A \rangle$ of polygons with this coordination. The amplitude of the deviation from the linear dependence is a measure of the randomness. The analysis of the patterns with Lewis' law is shown in Fig. 4. A linear relation is found in all stages, with deviations increasing from stage (i) to (iii).

3. Aboav's Law. The degree of angular correlation can be determined from Aboav's law,[7] which states that m_n, the average coordination of the neighbors of a drop with coordination number n, varies linearly with n^{-1}. The law is usually written in the form

$$nm_n = (6-a)n + c,$$

where a and c are constants. The character of the structure can be determined from the value of a (although there is no unique interpretation of this parameter[9]). Following Weaire and Rivier,[7] this parameter is larger than unity when the system tends to minimize the perimeter of the Voronoi polygons, that is when it minimizes distortion. This tendency implies that interior angles of 60° are favored, leading to orientational correlation. This would result in the appearance of six spots in the structure factor. The test of Aboav's law is shown in Fig. 5, where one sees that $a < 1$ in the states (i) and (ii), and exceeds unity in stage (iii). This is in accord with the behavior of the structure factor (Fig. 2).

4. Entropy. The degree of order in a structure can be described in terms of an entropy of conformation defined by

$$S = -\sum_n P_n \ln P_n.$$

This quantity is shown as a function of time in Fig. 1(c). It has a constant value during stage (i), falls smoothly during stage (ii), and approaches a constant value in stage (iii), in agreement with the other quantities.

[1] See, e.g., D. Beysens, D. Fritter, D. Roux, C. M. Knobler, and J. L. Viovy, in *Dynamics of Ordering Processes,* edited by S. Komura and H. Furukawa (Plenum, New York, 1988), p. 403.

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

[3] D. R. Nelson, M. Rubinstein, and F. Spaepen, Philos. Mag. A **46**, 105 (1982).

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

[5] See, e.g., V. M. Starov and N.V. Churaev, Kolloidn. Zh. **37**, 711 (1975).

[6] J. P. Marceroux, J.Prost, and H. Gruler, Nuovo Cimento D **3**, 204 (1984); M. Cloitre, Ph.D. thesis, University of Paris 6, Paris, 1989 (unpublished).

[7] See, e.g., D. Weaire and N. Rivier, Contemp. Phys. **25**, 59 (1984).

[8] F. T. Lewis, Proc. Amer. Acad. Arts. Sci. **77**, 149 (1949); N. Rivier and A. Lissowski, J. Phys. A **15**, L143 (1982).

[9] Lambert and Weaire [C. J. Lambert and D. Weaire, Philos. Mag. **47**, 445 (1983)] have constructed a model in which the parameter a can be alternatively related to the distribution of polygons. In this case a measures the deviation to a Gaussian distribution.
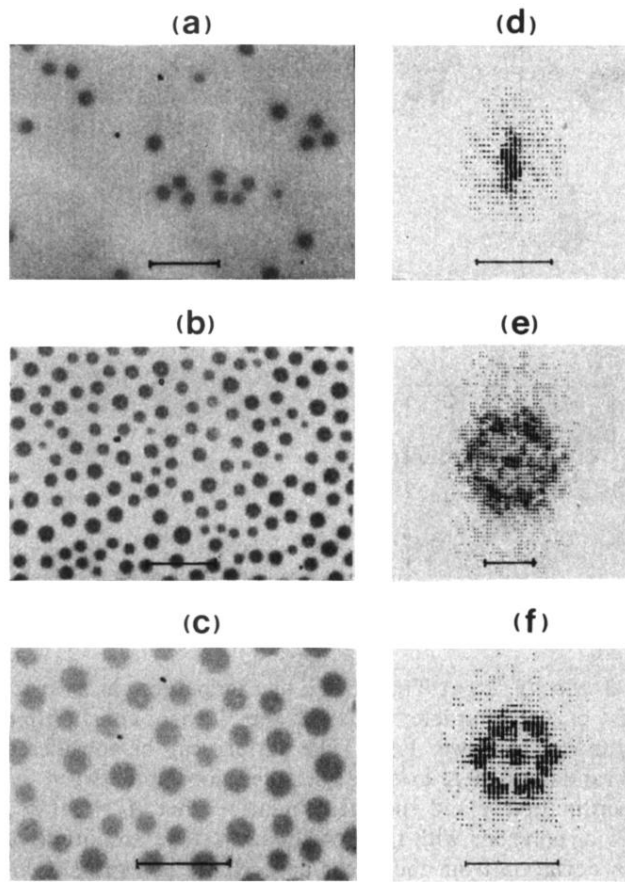
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