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Two-dimensional dendritic growth in Langmuir monolayers of D-myristoyl alanine

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We present a quantitative study of the *two-dimensional* dendritic growth of liquid-condensed domains observed by fluorescence microscopy in Langmuir monolayers of D-myristoyl alanine. The geometrical analysis of the dendrite tip region shows that the predicted relationship $\rho^2 V/d_0 D = \text{const}$ (V is the tip growth velocity, ρ the tip curvature radius, d_0 the capillary length, and D the diffusion coefficient) is reasonably verified. The determination of this constant yields an estimate of the line tension anisotropy.

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Amphiphilic monomolecular layers of fatty acids or phospholipids adsorbed at the air-water interface provide one of the best physical realizations of naturally two-dimensional (2D) systems easily accessible to nucleation and growth experiments. As the surface density is gradually increased, a succession of thermodynamical states is observed, and extended two-phase coexistence regions in the phase diagram have been detected early on by classical surface pressure measurements [1]. For instance, the first-order phase transitions between the liquid expanded (LE) phase and the various liquid condensed (LC) phases are signaled by a long plateau in the isotherms. However, it is only since the advent of direct visualization techniques, like fluorescence microscopy, that the rich variety of growth patterns has been revealed [2]. In particular, both stable and metastable growth shapes have been observed during isothermal compression experiments where an isolated LC domain grows within a continuous LE phase under supersaturation conditions [2,3]. In most cases, the diffusion-controlled growth of the LC phase leads to the formation of *isotropically* ramified patterns. This disordered, fractal-like, morphology is attributed, in agreement with x-ray-diffraction experiments [4], to the absence of long-range order in the LC phase. Unfortunately, this nonlinear growth regime can hardly be described analytically, and one is limited to the comparison of the Hausdorff exponent $df = 1.75 \pm 0.02$ [5] with the numerical prediction of the diffusion-limited aggregation model [6].

In this Rapid Communication, we present the first quantitative study on *dendritic* growth in Langmuir monolayers of long-chain amphiphiles with a chiral polar head. This chirality creates a microscopic order in the LC phase which in turn shows up in the anisotropic growth shape. Dendritic growth is peculiar in that it is steady state and is the only unstable growth regime which has been completely described theoretically [7]. It has been extensively studied in many three-dimensional (3D) systems [8]. However, Langmuir monolayers offer a case example to test the selection rules of the radius of curvature at the tip ρ and the growth velocity V in two dimensions [7–9]. We will also use the relationship between ρ and V to estimate the *line tension anisotropy* ϵ [9].

The D-myristoyl alanine (D-MAla) molecule differs from a fatty acid only by the chemical structure of its chiral polar head [10]. The experiments were done with the pure right-handed enantiomer, but the left-handed one gave strictly the same results. Since the D-MAla is not commercially available, it has been synthesized and purified (>99%) in our laboratory. The monolayers, containing 1 mol% of fluorescent dye NBD-HDA (Molecular Probes, USA), were spread onto an ultrapure (Millipore) water subphase at pH 2 in a thermostated trough. Monolayer compression rates $R = A^{-1} dA/dt$ ranged from 0.002 to 0.5 min^{-1} depending on the compression speed dA/dt (0.2–7 $\text{Å}^2\text{min}^{-1}$ per molecule) and the area per molecule A (120–25 Å^2). A metallurgical microscope (Reichert-Jung, Austria) equipped for epifluorescence and a Vidicon camera (Lhesa, France) were used for optical observations. Image digitization and processing were performed with a PIP board (Matrox Inc., Canada) and the Imagenia software (Biocom, France).

For temperatures above 16.5 °C, there is a well-defined first-order LE-LC transition in D-MAla monolayers for A values between 30 and 70 Å^2 [10]. By fluorescence microscopy, one observes the nucleation of the LC phase as dark, micron-size domains, randomly dispersed in the continuous LE phase (about one nucleation site per mm^2). There is a strong energy barrier, and for R higher than 1 min^{-1}, the first seeds nucleate 2 or 3 Å^2 per molecule after the coexistence has been entered. As the growth proceeds, these domains develop long dendritic branches. In order to maximize the length of these dendrites, we have performed two-step experiments, which allows us to separate the growth processes from the nucleation phenomena. Monolayer compression is first used to induce nucleation, but is stopped as soon as the first LC domains are observed optically. The area is then reincreased up to a value close to the coexistence region boundary. At this stage, the smaller islands melt away, and only a few seeds, roughly 5 μm in diameter and distant from each other by at least several millimeters, subsist. By compressing the monolayer again at low speed, these isolated seeds are forced to grow again, but additional nucleation is avoided. For R higher than 0.1 min^{-1}, dendritic growth is always observed. Figure 1 shows a typical dendritic domain ob-

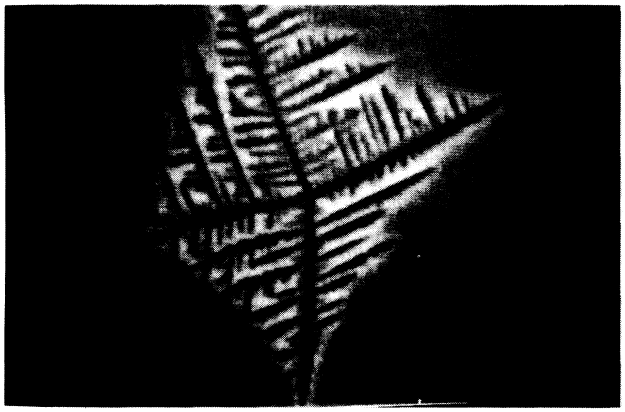
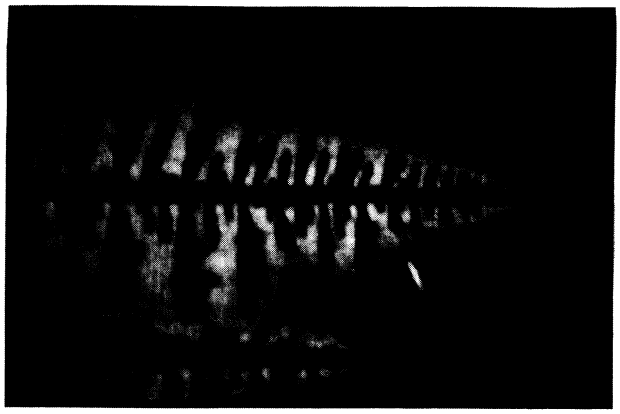


FIG. 1. Dendritic growth of a LC domain (dark) in a D-MAla monolayer observed by fluorescence microscopy. The fluorescent dye, expelled from the condensed phase, diffuses through the liquid expanded phase (bright). The horizontal size of the image is 600 μm.

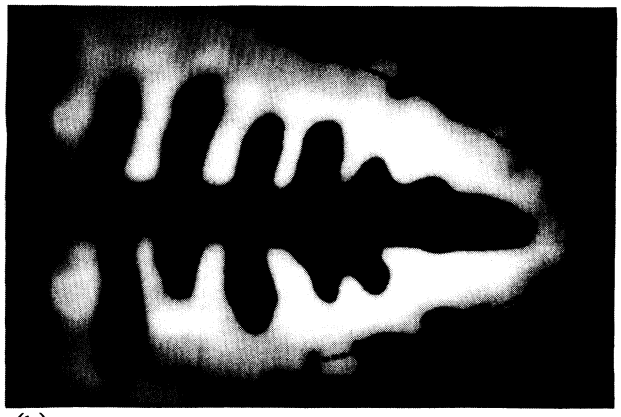
tained at $R \approx 3$ min^{-1}, a few seconds after the nucleation. This domain consists of four thin (< 10 μm wide) main branches of length ≈ 200–300 μm growing from the central nucleus. The tip velocity is several tens of μm s^{-1} and the radius of curvature at the tip ρ is so small that it is below the spatial resolution of our optical setup. By lowering R to less than 1 min^{-1}, one reaches smaller V values and the dendritic branches fatten to 10–15 μm. This can be seen in Fig. 2(a) which displays a dendrite grown at $R \approx 0.5$ min^{-1}. Fully developed dendrites can be one centimeter long. Several tens of secondary branches grow along their sides, making 60° or 90° angles, depending on the internal orientation of the main branch. They are spaced from each other by 10–20 μm, which is comparable with the main branch width. The mechanical behavior of these dendrites is solidlike: When they bump into each other, they hardly bend but they will break if the stress is large enough. If compression is stopped, sidebranch smoothing is observed, as expected for metastable shapes. This shape relaxation, however, is very slow, and the treelike shape subsists for many hours.

We have focused our attention on the two main properties of the dendrite tip region, namely, the parabolic shape predicted by Ivantsov [7], and the relationship between ρ, V, and the line tension anisotropy ϵ predicted by Ben Amar and Pomeau [9]. Because of the limited spatial resolution of our images, a direct comparison of the tip shape with a parabola was not possible. On the other hand, the 4 times enlargement of the dendrite tip region shown in Fig. 2(b), establishes that a contour line of equal brightness in the LE phase can be satisfactorily fitted to a parabola. These lines are the equipotential lines of the diffusion field, made visible by the dye molecule diffusing in the LE phase (see the bright halo around the dendrites in Figs. 1 and 2). Since the growth is steady state, they have to reflect the tip shape. This indirect procedure thus establishes that the dendrite tip is indeed parabolic.

We can now check the prediction that the product $\rho^2 V$ is a constant independent of V [7]. To determine ρ the simplest method is to measure directly the width X_0 of the



(a)



(b)

FIG. 2. (a) Dendrite grown for a compression rate of ≈ 0.5 min^{-1} (same scale as in Fig. 1). The bright halo around the dendrite corresponds to the diffusion gradient of the fluorescent dye in the LE phase. (b) The same tip region after a 4 times enlargement. This image has been electronically processed with an empirical brightness thresholding and contrast enhancement method which preserves the geometrical features of the patterns. A contour of equal brightness is signaled by a different grey scale. The numerical best fit with a parabolic profile is superimposed on the image.

main branch at a given distance Y_0 from its tip, and to use the general parabola equation for deriving $\rho = X_0^2/8Y_0$. Choosing $Y_0 = 10$ μm (i.e., 3 times higher than our resolution limit) allows us to assume that the first sidebranch is only a weak perturbation to the tip shape. In our experiments, X_0 ranged from 9 to 15 μm, and the corresponding ρ values from 1 to 3 μm (with an error of 20% to 80%), and V ranged from 2.5 ± 1 to 23 ± 1 μm s^{-1}. Figure 3 shows a plot of the calculated product $\rho^2 V$ vs V. We readily observe that $\rho^2 V$ is a constant, 25.9 ± 1.9 μm^3 s^{-1}, as expected [11].

It has been proved theoretically and experimentally in 3D systems that a prerequisite for dendritic growth is surface tension anisotropy [7–9]. For a 2D system, the theory tells us in addition that the line tension anisotropy ϵ is unequivocally related to the constant $\rho^2 V$. In the case of fourfold symmetry, one has a rigorous relation $\rho^2 V / d_0 D = \alpha \epsilon^{-7/4}$, where D is the diffusion coefficient in the LE phase, d_0 the capillary length, and α a numerical

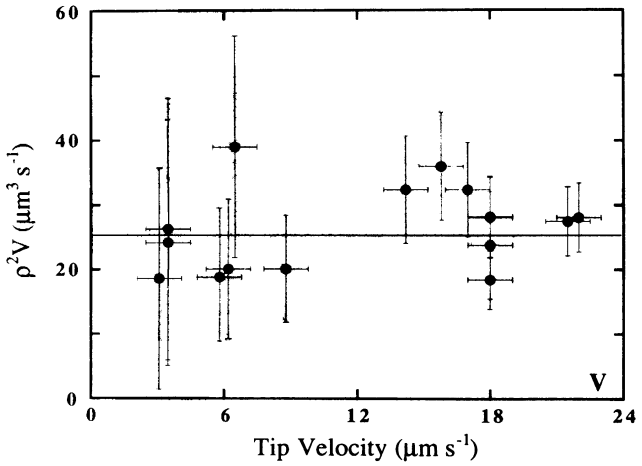


FIG. 3. ρ^2V vs V, where ρ is the radius of curvature at the dendrite tip and V the growth velocity. ρ^2V is a constant (the solid horizontal line shows the mean ρ^2V value $=25.9\pm1.9$ $\mu m^3 s^{-1}$) independent of V, in agreement with the theory.

coefficient [9]. Our observation of four main growth directions within a dendritic domain suggests that we can use this law to estimate ϵ for D-MAla monolayers. From experimental results obtained for fatty acids [5], d_0 can be estimated to be 4–30 times the molecular length a ($a\approx5.5$ Å since the molecular area of the LC phase is ≈30 Å^2), which gives $d_0\approx25$–200 Å. Taking $D\approx5\times10^{-7}$ cm^{2}s^{-1} [12], and our estimate of $\rho^2V\approx26$ $\mu m^3 s^{-1}$, we obtain $\rho^2V/d_0D\approx25$–200. Comparing this result with the theoretical master curve [9] yields an estimate of $\epsilon\approx(0.5$–$2.5)\%$. A more direct determination of ϵ in Langmuir monolayers has recently been obtained from the analysis of the equilibrium shape of 2D solid needles of NBD-stearic acid in coexistence with the gas phase [13]. In this particular case the ϵ value was found to be extremely large, about 0.9. This was interpreted as due to repulsive interactions between the inplane dipole moments carried by the molecules. For the D-MAla, ϵ is much weaker presumably because the dipoles are oriented perpendicular to the surface [14].

Finally, we have qualitatively studied the dependence of ρ and V on the diffusion coefficient D. In the LE phase, D scales as the inverse of the subphase viscosity η [15]. By using water-glycerol mixtures (30–70 vol%) for the monolayer subphase, we have been able to increase η, and thus decrease D by a factor of 2–100. We have observed that all qualitative geometrical features of the LE-LC phase transition stay the same as on pure water, but that the tip velocity *and* tip radius ρ decreased by increasing η at fixed R. This is in qualitative agreement with the theoretical prediction that ρ^2V/d_0D is independent of D. However, the hydrodynamic coupling between the amphiphile motions within the monolayer and the bulk flow in the subphase makes the dynamic behavior of Langmuir monolayers much more complex than in classical systems. In particular, it induces a wave-vector dependence of the cooperative diffusion coefficient which governs the dendritic growth.

To conclude, we have checked the recent theories of dendritic growth on a truly 2D system. Our estimation of the line tension anisotropy, made from the analysis of an out-of-equilibrium shape, falls in the range where 3D crystal growth experiments have also been successful. The observation of anisotropic growth in Langmuir films evidences that long-range microscopic order in the condensed phase can appear at the macroscopic scale. It is interesting to mention here that we have observed different growth shapes for compression rates smaller than 0.1 min^{-1}. Independent observations of dendritic growth involving different molecules have also been reported by three other groups [16]. Synchrotron x-ray diffraction studies are now in progress in our laboratory in order to check if they correspond to different macroscopic structures. For these highly asymmetrical molecules, there also may be some influence of the interfacial kinetics, which could be noninstantaneous and depend on the molecular orientation.

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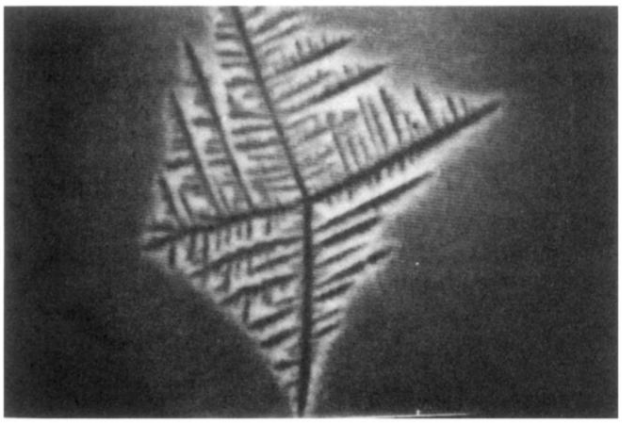

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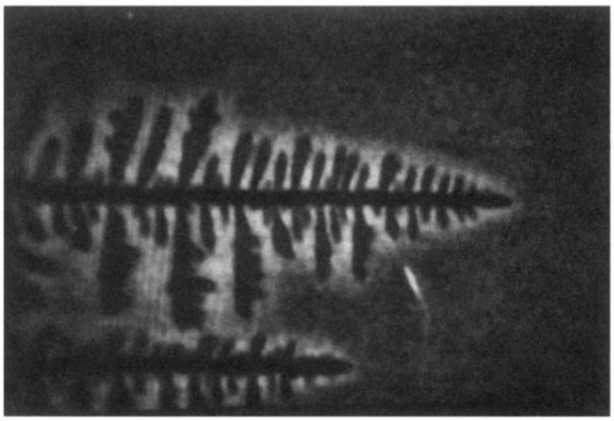
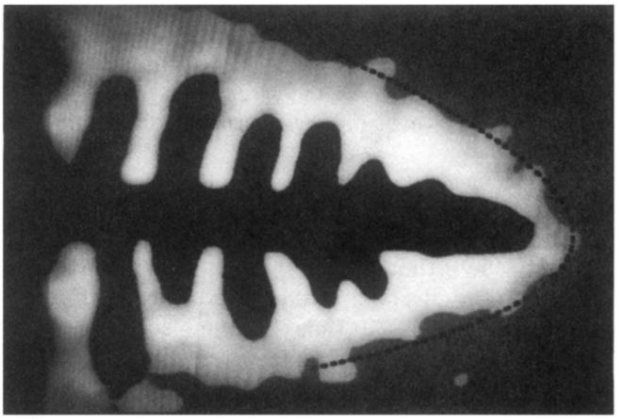


(a)



(b)

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