DC, 1984), pp. 319–328.
31. The only known processes that could lead to different signals are (i) the effect of CO_2 exchange with the atmosphere, which would modify ^{13}C while leaving Cd unchanged; and (ii) increases in the relative percentage of decaying Antarctic organisms, which are more depleted in ^{13}C than organisms in other parts of the ocean. Mechanisms that are not observed in the modern ocean but which might imaginably cause $\delta^{13}C$ and Cd offsets include (iii) large changes in fractionation of $\delta^{13}C$ by organisms; (iv) the formation of organic matter with C:Cd ratios that are very different from modern organisms; or (v) the local oxidation of a carbon source lacking Cd (for example, cellulose). None of these latter options seems very probable.
32. J. C. Duplessy *et al.*, *Paleoceanography* **3**, 343 (1988).
33. E. A. Boyle and L. D. Keigwin, *Science* **218**, 784 (1982); W. Curry and G. P. Lohmann, *Nature* **306**, 577 (1983); D. Oppo and R. G. Fairbanks, *Earth Planet. Sci. Lett.* **86**, 1 (1987); W. B. Curry, J. C. Duplessy, L. D. Labeyrie, N. J. Shackleton, *Paleoceanography* **3**, 317 (1988).
34. M. E. Raymo, W. F. Ruddiman, N. J. Shackleton, D. W. Oppo, *Earth Planet. Sci. Lett.* **97**, 353 (1981).
35. L. D. Keigwin and E. A. Boyle, *Paleogeog., Paleoclimatol., Paleoecol.* **73**, 85 (1989); L. D. Labeyrie and J.-C. Duplessy, *ibid.* **50**, 217 (1985).
36. N. Kallel *et al.*, *Nature* **333**, 651 (1988).
37. L. H. Chan, J. M. Edmond, R. F. Stallard, B. Grant, *Deep Sea Res.* **24**, 613 (1977).
38. D. W. Lea, thesis, Massachusetts Institute of Technology (1989); D. W. Lea and E. A. Boyle, Paleoceanography, in press; Nature, in press.
39. W. S. Broecker and T.-H. Peng, *Tracers in the Sea* (Eldigio, Palisades, NY, 1982).
40. ______, S. Trumbore, G. Bonani, W. Wolfli, *Global Biogeochem. Cycles* (in press); N. J. Shackleton, J.-C. Duplessy, M. Arnold, P. Maurice, M. A. Hall, J. Cartlidge, *Nature* **335**, 708 (1988).
41. W. S. Broecker, *Paleoceanography* **4**, 213 (1989).
42. J. Imbrie, A. McIntyre, A. Mix, in *Climate and Geosciences*, A. Berger, S. Schneider, J. Duplessy, Ed. (Klüwer, Dordrecht, 1989), pp. 121–164.
43. A. L. Berger, *Quat. Res.* **9**, 139 (1978).
44. J. Imbrie *et al.*, in *Milankovitch and Climate, Part 1*, A. L. Berger, J. Imbrie, J. Hays. G. Kukla, B. Salzmann, Eds. (Reidel, Dordrecht, 1984), pp. 269–305.
45. L. D. Keigwin and G. A. Jones, *Deep-Sea Res.* **36**, 845 (1989).
46. E. A. Boyle and L. D. Keigwin, *Nature* **330**, 335 (1987).
47. S. Manabe and R. J. Stouffer, *J. Clim.* **1**, 841 (1988).
48. E. Maier-Reimer and U. Mikolajewicz, *Max-Planck-Inst. Meteorol. Rep. 39* (1989).
49. The author's studies of deep water paleoceanography has been funded by National Science Foundation grants, most recently grant OCE-8710168. I thank Alan Mix and an anonymous reviewer for constructive comments on the first draft of this manuscript.

Seeing Phenomena in Flatland: Studies of Monolayers by Fluorescence Microscopy

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Monolayers formed at the interface between air and water can be seen with fluorescence microscopy. This allows the phase behavior of these monolayers to be determined by direct observation and opens up the possibility of following the kinetics of phase transformations in two-dimensional systems. Some unexpected morphologies have been discovered that provide information about the nature of monolayer phases and have connections to pattern formation in other systems.

RESEARCHERS HAVE LONG BEEN INTRIGUED THAT BY ALMOST trivial means (*1*) one can produce a monolayer—a structure only a single molecule thick—at the interface between air and water. Monolayers formed by substances that are insoluble in the liquid subphase are called Langmuir monolayers. These are distinguished from Gibbs monolayers, which result from the preferential adsorption at an interface of substances that are soluble in the bulk, and Langmuir-Blodgett films, which are formed when Langmuir monolayers are transferred to solid substrates.

The amphiphilic molecules that form Langmuir monolayers have hydrophilic and hydrophobic portions, and it is the balance between these opposing natures that keeps the molecules at the surface. Long-chain fatty acids are typical monolayer-formers; their carboxyl head groups remain immersed in the water while their hydrocarbon tails limit their solubility. Chains longer than about 12 carbons are necessary to keep the solubility low but, if the hydrophobic character of the chain is dominant, the substance will form a lens rather than a monolayer on the surface.

Life scientists have investigated phospholipid Langmuir monolayers in order to gain insight into the structure and properties of bilayers, which serve as models for cell membranes. More recently, the resurgence of interest in complex fluid systems that are composed of amphiphiles (emulsions, microemulsions, and lamellar systems) has stimulated monolayer research. (It is interesting that much of what was once called colloid chemistry is now seen regularly in the condensed-matter sections of journals such as *Physical Review Letters*.)

The desire to investigate the effect of dimensionality on the equilibrium and dynamic properties of physical systems has also stimulated monolayer experiments. I began to study Langmuir monolayers in order to extend my research on the kinetics of phase transitions in fluid mixtures to two-dimensional systems. This goal has not yet been realized, in part because the experimental problems are more significant than I had realized, but mostly because we have been sidetracked by the discovery of a rich variety of unexpected phenomena. It is these phenomena that will be the focus of this article.

Phase Behavior of Langmuir Monolayers

One prepares Langmuir monolayers (*2, 3*) by depositing a solution of an amphiphile in a volatile solvent onto a clean water surface; the monolayer spreads spontaneously as the solvent evaporates. If the solubility of the amphiphile in the subphase is negligible, a monolayer can be thought of as a separate phase with thermodynamic properties analogous to those of three-dimensional (3-D) systems. The pressure p is replaced by a surface pressure π, and the volume V becomes the area A. A barrier can be moved across the surface of the water to change the area available to the

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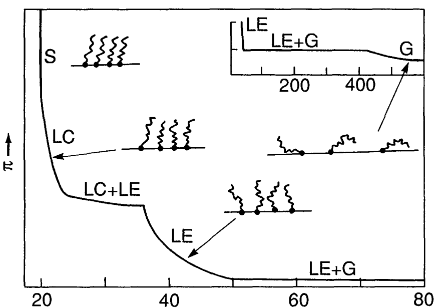

Fig. 1. Schematic Langmuir monolayer isotherm, a plot of surface pressure (π) against the area (A) per molecule at constant temperature. The areas at which the changes in slope occur correspond roughly to those found for a fatty acid such as PDA at room temperature. The inset shows the LE + G transition region at high areas. The cartoons indicate the microscopic differences between the phases.

monolayer (in much the same way that a piston can be used to compress a 3-D system), and one can determine the surface pressure by measuring the force per unit length on a float or thread separating the monolayer from a clean surface.

The behavior of the monolayer may depend on properties of the subphase. For example, the charge on the head group may change when the pH or ionic strength of the water is altered. But if the properties of the subphase are held constant and measurements are carried out at constant p, there is an exact correspondence between the equation of state for a pure monolayer, $\pi = \pi(A, T)$, and that for a one-component, 3-D system, $p = p(V, T)$ (where T is temperature).

The determination of π, A isotherms is the most common measurement that is performed on Langmuir monolayers, and much of our knowledge of the phase behavior of monolayers has been inferred from such studies. The schematic isotherm shown in Fig. 1 is typical of many amphiphiles.

Langmuir monolayers are gaseous (G) where the area per molecule is large compared to the molecular dimensions. In the G phase, the hydrocarbon portions of the molecules make significant contact with the surface. (The interaction with the water surface is attractive, even for the hydrophobic tail.) The long plateau that arises when the gas is compressed is associated with a transition to a liquid phase, often called the liquid-expanded (LE) phase. [We expect a plateau because the phase rule for insoluble monolayers has essentially the same form as that for 3-D systems (*3*): when there are two phases present, a pure monolayer has only one degree of freedom, and fixing the temperature fixes π.] In the LE phase, the hydrocarbon chains lift from the surface but remain largely disordered.

Further compression leads to a transition to a phase that has been called liquid-condensed (LC). The isotherm in this transition region has been drawn with a marked slope, as found in most isotherm measurements. The fact that the plateau is not horizontal suggests that the LE-LC transition is not first-order, but this view has been disproved by a number of recent measurements (*4*).

Despite its name, the LC phase is not a liquid. In the LC phase, the degree of chain alignment and the number of *trans* conformations are higher than in the LE phase, and there is evidence of long-range order. The kink in the isotherm at higher compressions is attributed to a transformation from the LC phase to another phase, taken to be an ordered, 2-D solid. In this steepest part of the isotherm, the area per molecule corresponds closely to the packing of chains found in 3-D crystals of the amphiphile.

A T, A phase diagram can be constructed when isotherm measurements are performed at several temperatures. The schematic diagram shown in Fig. 2 seems to apply to many amphiphiles, with the T and A axes shifted to account for the energy and size parameters characteristic of each molecule (*2*). For example, the 25°C isotherm for octadecanoic acid would correspond to one for pentadecanoic acid (PDA) near 0°C.

Studies of a variety of other macroscopic properties (*2*, *3*), such as the surface potential and the viscosity, as well as packing arguments have been useful in interpreting the isotherms and characterizing the monolayer phases. This work has been augmented by recent experiments with new techniques, such as x-ray and neutron scattering and reflectivity, second-harmonic generation, and sum-frequency spectroscopy, that provide more detailed information about the microscopic nature of the monolayer phases (*4*).

Fluorescence Microscopy of Langmuir Monolayers

None of the classical or the more modern diffraction and spectroscopic methods provides direct information about the morphology of Langmuir monolayers. However, relatively simple measurements by fluorescence microscopy allow direct observation of the textures of Langmuir monolayers (*5*–*7*) and open up a whole new class of investigations. A monolayer containing a small amount of a fluorescence is prepared in a trough on the stage of a microscope. The fluorescent probe is excited with a laser or an arc lamp, and images of the monolayer are detected with a high-sensitivity television camera and recorded on videotape for subsequent analysis. Figure 3 shows the images obtained when a monolayer of PDA containing about 1% of the probe 4-(hexadecylamino)-7-nitrobenz-2-oxa-1,3-diazole (NBD-hexadecylamine) is compressed at 25°C.

The monolayer was prepared at a molecular area of 61 Å^2 molecule^{-1}; according to the isotherm measurements, this area corresponds to the G-LE two-phase region. In this state, the image of the monolayer (Fig. 3A) consists of dark circular "bubbles" of gas in the white field of the LE phase. The contrast between the phases is attributable to the difference in density and, perhaps, to quenching of the probe fluorescence when it is in the G phase.

If the density of the monolayer is increased, either by compression or by addition of PDA at constant area, the amount of gas decreases (Fig. 3B) until at a sharply defined area one obtains a completely white field (Fig. 3C). All of the monolayer is now in the LE phase. This one-phase region persists as the area per molecule is decreased, until dark circular domains of the LC phase abruptly appear (Fig. 3D). (In this case, the difference in contrast reflects the low solubility of the probe in the LC phase.) The transition from LE to

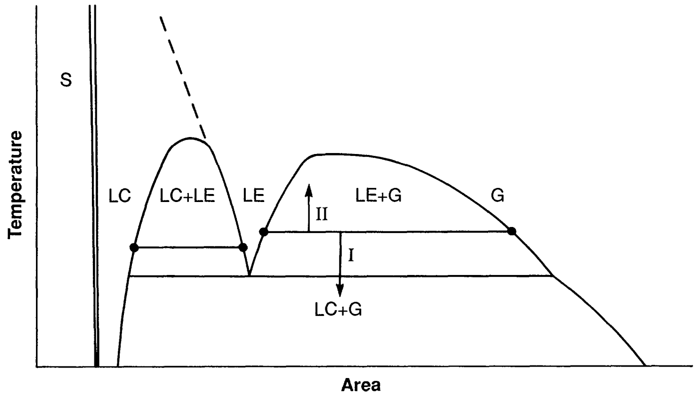

Fig. 2. Schematic temperature-area diagram. The width of the LC-LE coexistence region is highly exaggerated as compared to the LE-G region. Both coexistence curves are shown terminating in critical points, but there is no convincing experimental evidence that an LC-LE critical point exists. Horizontal lines are tie lines that connect coexisting phases. The dashed line represents a second-order transition that would be expected to intersect the coexistence curve if the LC and LE phases were not of the same symmetry. The arrows labeled I and II that extend from tielines show the paths followed in experiments described in the text.

LC phase is clearly first order. The fraction of LC phase grows with increasing density (Fig. 3E), and, if the probe concentration is very low, one can detect the termination of LE-LC coexistence by the complete loss of the bright LE regions.

One can explore the monolayer phase diagram by locating the transition points, either by compression and expansion along an isotherm or by heating and cooling along an isochor. By measuring the area fraction of each phase as a function of the average area per molecule, one can calculate the molecular areas of the coexisting phases from the "lever rule" (*8*). These techniques were used by Moore *et al.* (*9*) to investigate the phase diagram of PDA.

Langmuir monolayers of PDA have been studied repeatedly and with unusual care (*10, 11*), but not without controversy. Highly precise isotherm measurements in the G-LE plateau region had shown (*10*) that there was a non-zero slope in the isotherms above 26.3°C, meaning that there was a G-LE critical point at this temperature but another precise study (*11*) found that the isotherms were horizontal at least to 40°C, the highest temperature at which the measurements could be carried out. The fluorescence experiments do not explain the reasons for the disagreement between these two studies but show clearly that G-LE equilibrium persists to the higher temperature.

A question that must be faced with every probe method is, "What is the effect of the probe?" The probe is an impurity that does not have the same solubility in each phase and therefore must shift the phase boundaries. However, it can be shown for PDA that the changes in the phase boundaries are of the order of the uncertainties in the boundaries determined from the isotherm measurements (*9*). There is remarkably good agreement between the isotherm and fluorescence data.

The black-and-white character of the fluorescence image would seem to limit the utility of fluorescence microscopy to two-phase equilibria. By observing the evolution of features in the image, however, it is possible to examine transitions involving more phases. For example, if a PDA monolayer that is originally in the G-LE two-phase region is cooled at constant area to a temperature below 17°C (the path indicated by arrow I in Fig. 2), the pattern shown in Fig. 3F is observed. New dark circular domains appear, each of which is ringed by small dark "bubbles"; these new features grow with time at the expense of the LE phase. The new circular domains can be identified as the LC phase and the bubbles as the G phase. They form because the monolayer has been cooled below the G-LE-LC triple point into the G-LC two-phase region. If the system reached equilibrium, there would be no LE phase, but the transformation goes to completion only very slowly. Moore *et al.* have shown (*9*) that the temperature at which the LC phase first appears upon cooling or disappears upon heating is in excellent agreement with values of the triple-point temperature obtained from isotherms.

Patterns and Dynamics: 2-D Foams

The morphologies observed in Fig. 3 are not remarkable. They are what one might expect for the nucleation and growth of phases in the gravity-free environment of a monolayer. The driving force for coalescence of domains in the monolayer is the tendency to minimize surface energy by reducing interfacial length and curvature, which is weak compared, say, to the effect of gravity in segregating fluids of different densities (*12*).

We were surprised to discover (*7*) the existence of a different transient morphology in the G-LE two-phase region: a random network structure, which has the appearance of a 2-D foam. This structure is observed when the solvent evaporates or when there is rapid expansion from the LE phase into the G-LE coexistence region.

As the gas bubbles that nucleate in the LE phase grow, the fluid layers between them become thinner, and the droplet curvature decreases. As a result, the pattern of circular bubbles is converted into a polygonal network of cells in which the sides meet at threefold vertices (Fig. 4A). Such 2-D networks are ubiquitous: they are found in magnetic films, in the pattern of grain boundaries on the surface of a metal, in geological formations, and in biological structures (*13*).

Are the similarities among these network structures more than superficial? Despite the very different nature of the media in which the networks form, do the patterns evolve according to some universal laws, and are their structures the same? To answer such questions we must first be able to describe the network. This can be accomplished (*13*) in terms of statistical quantities such as the average cell size, the probability distribution of polygons according to their numbers of sides, and the correlation between the number of sides of a polygon and the average number of sides of its neighbors.

One can determine these characteristics by recording the evolution of the network on videotape and analyzing digitized images. Such studies (*14*) show that monolayer foams are in many respects quantitatively similar to other 2-D networks. For example, the

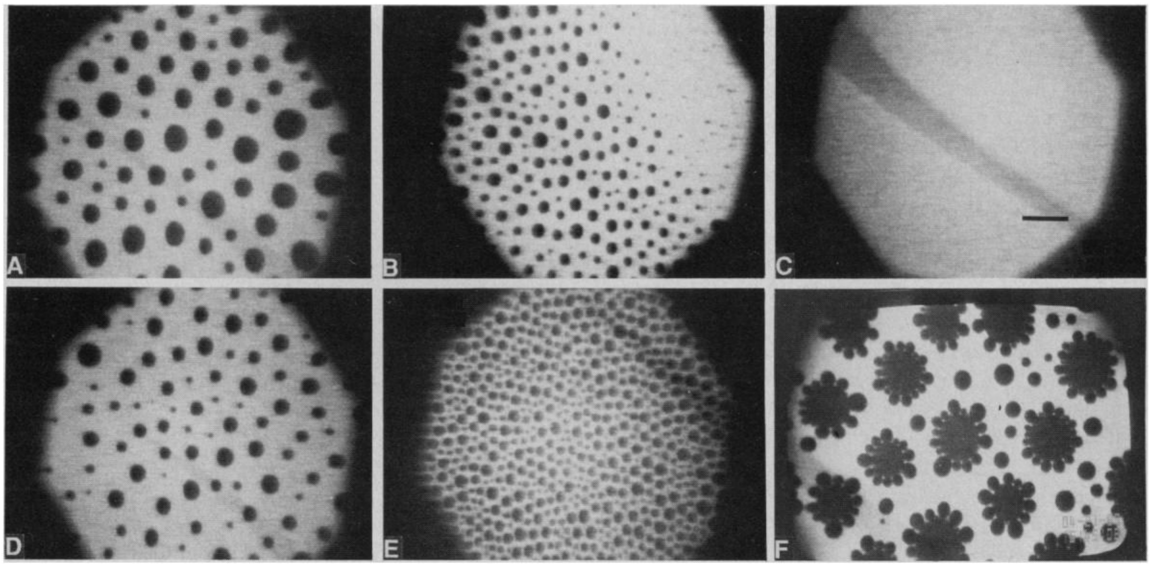

Fig. 3. (A–E) Fluorescence microscope images obtained when PDA is compressed from 61 to 19 Å^2 molecule^{-1} at 25°C: (**A**) 61 Å^2 molecule^{-1}; (**B**) 50 Å^2 molecule^{-1}; (**C**) 36 Å^2 molecule^{-1} [the line in (C) represents 100 μm]; (**D**) 27 Å^2 molecule^{-1}; (**E**) 24 Å^2 molecule^{-1}; (**F**) three-phase coexistence observed after a temperature quench to a temperature below the triple point. The quench began with the monolayer in the G-LE coexistence region at an area of 51 Å^2 molecule^{-1}, and the path followed is indicated by arrow I in Fig. 2.

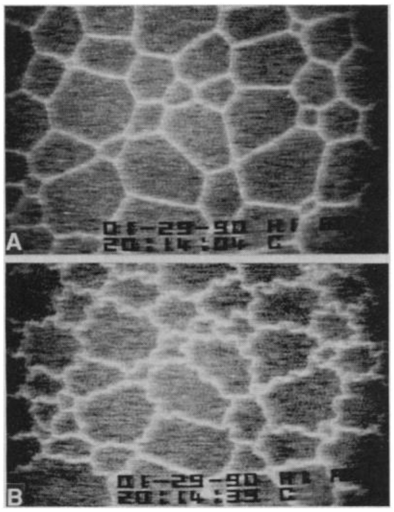

Fig. 4. (**A**) Network structure obtained upon expansion of the LE phase at constant temperature. (**B**) Buckling instability observed when a foam of ethyl heptadecanoate was heated along path II shown in Fig. 2.

average cell perimeter is a linear function of the number of sides. This relation is also found for soap foams trapped between plates, and for grain boundaries. It appears very likely that the properties of such networks are universal.

If there were no probe, would the foam exist? It is known that in 3-D systems, pure, one-component fluids do not foam (*3*). We believe that the network structure is intrinsic to the monolayer. A key requirement for the formation of such a network is the resistance of the cell sides to becoming so thin that they break. There are many examples in monolayers of the formation of stable linear structures. Such linear features arise because amphiphile molecules are dipolar, and in condensed monolayer phases they are substantially aligned perpendicular to the surface and are always oriented with the head group at the subphase surface.

Because of this imposed geometry, the dipoles repel each other and the dipolar energy can be minimized if the dipoles form extended linear structures. This tendency is counterbalanced by the line tension between the phases, which tends to minimize the perimeter and keeps the array intact. Calculations of the free energy of monolayer phases (*15*) show that the width of the linear structures depends on the quantity exp $(\sigma/\Delta\mu^2)$, where σ is the line tension between the phases and $\Delta\mu$ is the difference in dipole density.

A Buckling Instability

The evolution of the network structure shown in Fig. 4A occurred at constant temperature. If the temperature is raised after the network structure has formed (*16*), we may see the phenomenon shown in Fig. 4B. As the heating begins, the cell sides thicken slightly and then suddenly buckle. The explanation of this buckling instability ties together the structure with the thermodynamic and kinetic behavior of Langmuir monolayers.

Although the buckling can be explained in terms of a time-dependent Ginzburg-Landau theory (*16*), it can also be understood as an Euler instability (*17*). This kind of instability arises when a thin metal rod is compressed along its axis. If the compressive force exceeds some critical value, the rod suddenly bows. In the case of the monolayer, the compression is caused by a combination of circumstances.

1) Because the overall density of the monolayer is greater than the density at the G-LE critical point, when the two-phase system is heated along a path indicated by arrow II in Fig. 2, the amount of the LE phase must increase in accord with the lever rule.

2) Because the width of the cell sides is fixed by balance between the dipolar density and the line tension, if the area of the LE phase is to increase, it can do so only by a lengthening of the cell sides.

3) Because the cell sides are locked into the foam network, the increase in length is initially accommodated by compressing the fluid until, at a critical compression, the sides lengthen by buckling.

However, the instability in the foams is not simply a bowing of the sides. The change in length is accommodated by a shorter wavelength instability. Wavelengths shorter than half of the side length can arise only if there is a mechanism by which an energetic price must be paid for the amplitude of the instability. In the case of the monolayer networks, the dipole repulsion between the cell sides plays this role.

To estimate this effect, we can model the network as an infinite array of parallel lines of dipoles. From this model, we find that the wavelength of the instability should be proportional to the spacing between the sides, which we can take as the average cell size. Experiments (*16*) confirm this dependence.

Complex Patterns

Complex patterns also appear at the LE-LC transition. When a fatty acid or phospholipid monolayer is driven rapidly into this two-phase region, either by compression or by a rapid temperature quench, the LC domains are no longer compact but have instead a ramified morphology (Fig. 5A). These structures look very much like the fractal patterns obtained by the process of diffusion-limited aggregation (*18*). They are not equilibrium forms; they "heal" into circular domains if the compression is stopped or the temperature is held constant.

It seems likely that the fractal patterns are linked to the presence of the probe. Studies of the growth of such patterns in the phospholipid dimyristoylphosphatidylethanolamine (*19*) have shown that they occur by the mechanism of constitutional supercooling. As the LC phase condenses, probe accumulates at the interface and diffuses away into the LE phase; the transition pressure increases with increasing probe concentration. Thus, as the monolayer is compressed, regions of the interface in which the probe concentration is low convert to LC phase while the regions of higher probe concentration are still in the LE phase. Steep concentration gradients increase the rate of diffusion of the probe away from the interface, so these are regions in which the LC phase preferentially grows.

Although the probe may induce the instability, we may still derive information about the monolayer by examining the conditions under which the pattern forms. We have observed in ethyl and methyl esters of some fatty acids that the pattern changes from the open fractal structure at high temperature to a more compact, dendritic form at low temperature (Fig. 5B).

The two types of patterns grow in distinctly different ways. The open structure grows by tip splitting, in which the tips of the arms split repeatedly. In the dendritic structure, the tip remains stable as the arm grows and branches grow along the sides. Dendritic growth occurs only when there is an anisotropy in line tension between the phases, that is, only if the line tension is different in different directions of growth (*18*). Such an anisotropy reflects an underlying order in the LC phase, an order that is not present at higher temperature.

Thus, the existence of the dendritic structure demonstrates that the LC phase is not an isotropic liquid. Although we do not know the nature of the order in these esters, x-ray scattering measurements on LC phases in other systems (*4*) show that they are orientationally ordered but have little translational order. (The translational correla-

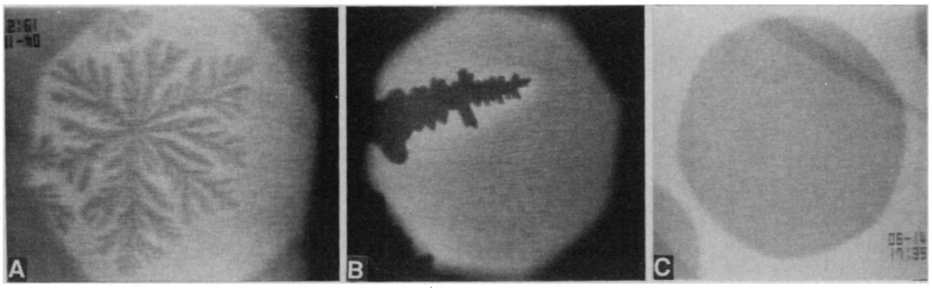

Fig. 5. Nonequilibrium patterns in ester monolayers at the LC-LE transition. (**A**) Fractal pattern in which the growth is by tip splitting, and (**B**) dendritic pattern in which the tip is stable and side branching occurs in ethyl octadecanoate monolayers. (**C**) Equilibrium hexagonal morphology observed in ethyl heptadecanoate monolayers.

tion length is less than 100 Å.) It is therefore reasonable to assume that this is the case in our experiments.

The anisotropy of the LC phase in ester monolayers can also be demonstrated by equilibrium studies. Circular LC domains in ethyl heptadecanoate monolayers undergo a reversible transition to a hexagonal shape when they are cooled (Fig. 5C). The domains have the form expected for 2-D crystals, which should have flat sides only at absolute zero. Here again, we cannot tell the nature of the underlying order from our macroscopic observations; we know only that there is sixfold symmetry and that the range of the order is about one million times the intermolecular separation.

The sharp, reversible change from circular to hexagonal domains and the change in the nonequilibrium patterns suggest that we are observing a phase transition. In fact, Lundquist (*20*) proposed that, at low temperatures, the LE phase coexists with a phase labeled L_2', in which the chains are tilted with respect to the surface, and that, at high temperatures, the L_2' phase undergoes a transition to the "super-liquid" (LS) phase, in which the chains are vertical. The transition temperatures that we observe are in accord with those at which there is a changeover from L_2'-LE coexistence to LS-LE coexistence.

Lundquist identified three more condensed phases in esters; similar phase diagrams involving half a dozen condensed phases had previously been inferred from isotherm studies on fatty acids (*21*). Recent x-ray studies (*22*) confirm the existence of five distinct condensed phases in a fatty acid. It is evident that the phase diagram sketched in Fig. 2 is highly oversimplified.

Conclusions

Fluorescence microscope investigations of Langmuir monolayers have uncovered a rich variety of phenomena. The film morphologies observed, and the way in which these morphologies evolve, can provide information about the nature of monolayer phases. Because of the uniaxial alignment of the molecules that is imposed by the pinning of the amphiphile head group to the subphase surface, dipolar forces play an important role in determining the patterns and instabilities, but the other interactions within the monolayer cannot be neglected. It has become clear from structural studies and simulations that the van der Waals interactions between chains, the chain conformations, and the head group interactions all play roles in determining the character of the phases of these monolayers. A full understanding of Langmuir monolayers will require a combination of many tools, with fluorescence microscopy among them.

REFERENCES AND NOTES

1. C. M. Knobler, M. E. Holzer, E. R. Hardwick, *Laboratory Experiments in General Chemistry* (Burgess, Minneapolis, 1977), experiment 13.
2. G. L. Gaines, Jr., *Insoluble Monolayers at Liquid-Gas Interfaces* (Wiley-Interscience, New York, 1966).
3. A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, ed. 4, 1982).
4. For a review of recent developments, see C. M. Knobler, *Adv. Chem. Phys.* 77, 397 (1990).
5. V. von Tscharner and H. M. McConnell, *Biophys. J.* **36**, 409 (1981).
6. M. Lösche, E. Sackmann, H. Möhwald, *Ber. Bunsen-Ges. Phys. Chem.* **87**, 848 (1983); M. Lösche and H. Möhwald, *Rev. Sci. Instrum.* **55**, 1968 (1984).
7. B. G. Moore, C. M. Knobler, D. Broseta, F. Rondelez, *J. Chem. Soc. Faraday Trans. 2* **82**, 1753 (1986).
8. G. W. Castellan, *Physical Chemistry* (Addison-Wesley, Reading, MA, ed. 3, 1983), p. 299.
9. B. G. Moore, C. M. Knobler, S. Akamatsu, F. Rondelez, *J. Phys. Chem.* **94**, 4588 (1990).
10. M. W. Kim and D. S. Cannell, *Phys. Rev. A* **13**, 411 (1976).
11. N. R. Pallas and B. A. Pethica, *J. Chem. Soc. Faraday Trans. 1* **83**, 585 (1987).
12. Coalescence is also inhibited by repulsion between domains of aligned dipoles, an effect described later.
13. D. Weaire and N. Rivier, *Contemp. Phys.* **25**, 59 (1984).
14. K. J. Stine, S. A. Rauseo, B. G. Moore, J. A. Wise, C. M. Knobler, *Phys. Rev. A* **41**, 6884 (1990); B. Bergé, A. J. Simon, A. Libchaber, *ibid.*, p. 6893.
15. H. M. McConnell and V. T. Moy, *J. Phys. Chem.* **92**, 4520 (1988); H. M. McConnell, *Proc. Natl. Acad. Sci. U.S.A.* **86**, 3452 (1989).
16. K. J. Stine, C. M. Knobler, R. C. Desai, unpublished work.
17. L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, New York, 1970).
18. T. Vicsek, *Fractal Growth Phenomena* (World Scientific, Singapore, 1989).
19. A. Miller and H. Möhwald, *J. Chem. Phys.* **86**, 4258 (1987).
20. M. Lundquist, *Chem. Scr.* **1**, 197 (1971).
21. S. Ställberg-Stenhagen and E. Stenhagen, *Nature* **156**, 239 (1945).
22. B. Lin, T. M. Bohannon, M. C. Shih, P. Dutta, *Phys. Rev. Lett.* **65**, 191 (1990).
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