SURFACE PHYSICS

A vanishing interface

Philip Ball

THE distinction between a continuum and a molecular description is what, in large part, divides dynamical and statistical-mechanical (equilibrium) theories of fluid behaviour. A recent meeting* bore the good news that in surface and colloid science, where the molecular-scale details can seldom be ignored, this divide between statics and dynamics is narrowing. For chemical engineers a dynamical viewpoint has always seemed natural, of course: their concern has long been with problems of flow, rheology, dynamical instabilities. But it is reassuring that the microscopic theories now being brought to bear on these issues are, on the whole, equal to the challenge.

An obstacle to fundamental (as distinct from empirical) understanding of surface dynamics is the difficulty of realizing experimentally the idealized conditions that the theories must take as their starting point. The vagaries of a liquid droplet spreading on a surface (such as hysteresis, for advancing and receding droplets, in the angle of contact between the air–liquid and solid–liquid interfaces, or pinning of the 'contact line' at the film's edge to surface imperfections) are a useful measure of surface characteristics for engineers, but the bane of physicists trying to understand how spreading occurs.

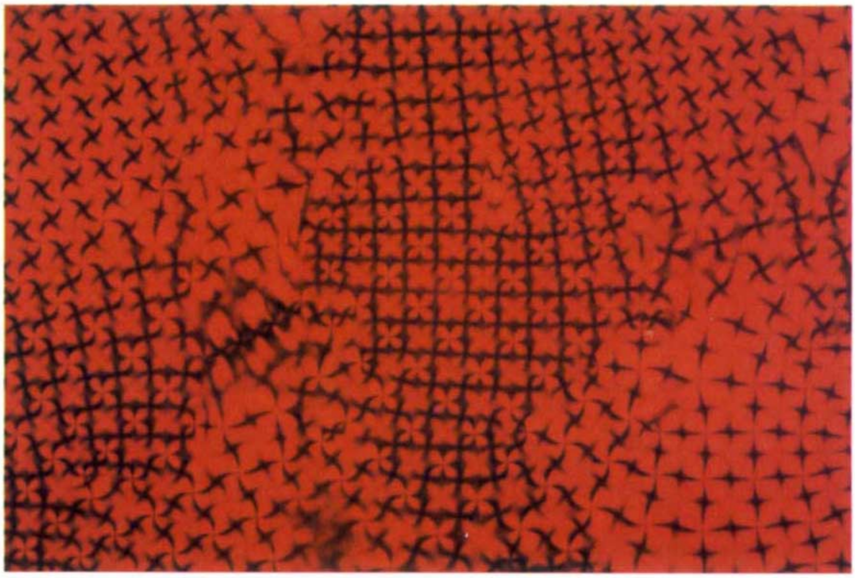
For a liquid spreading on perfectly smooth, uniform surfaces, a hydrodynamical analysis predicts proportionality between the cube of the contact angle θ and the velocity of the advancing contact line. But real surfaces are seldom so ideal: J. F. Joanny (Institut Charles Sadron, Strasbourg) described how this spreading behaviour should be modified by surface defects. A contact line that becomes snagged on these is somewhat like a string under tension, but softer. A string relaxes harmonically when deformed and released, with a relaxation time τ proportional to the inverse square of the wavevector of deformation q. For the contact line, on the other hand, deformation affects also the two-dimensional liquid–air interface, with the result that surface point defects induce a smooth deformation and τ varies with the inverse of q.

T. Ondarçuhu and M. Veyssié (Collège de France) have now devised a way to test this prediction experimentally[1]. They generate a homogeneous surface with a specified surface energy by coating a silicone wafer with long-chain aliphatic or fluorinated silanes, and introduce a deformation of a single wavelength by merging a linear liquid front (silicone oils are used) with regularly spaced circular droplets. When gravitational effects are not important (that is, when q is not too small), the theory is vindicated: an encouraging basis on which an understanding of real-world spreading can develop.

The driving force behind droplet spreading on a horizontal surface (when the film thickness is not so large that gravity plays a part) is the lowering of surface energy, which is decreased when the substrate is either partly or totally covered by the liquid film (respectively partial or complete wetting). In the former case, a liquid film spread forcibly over the entire surface will retract to the equilibrium configuration in which parts of the surface are exposed again. This 'dewetting' process, relevant for example to the problem of keeping windscreens free from obscuring liquid films, also obeys the θ^3 dynamics[2] (C. Redon, Université Pierre et Marie Curie).

If the spreading rate is increased by driving the flow using, for example, gravitational[3] or centrifugal[4] forces, a linear contact line becomes unstable even in the absence of surface heterogeneity. A fingering instability with a well-defined wavelength then develops spontaneously[3], as seen in the 'tears of wine' that form in a partly filled glass (A. M. Cazabat, Collège de France). The Marangoni effect — flow induced by gradients in surface tension — can also produce an instability. Surface-tension gradients can be created, for example, by imposing a temperature gradient on the flow[5] or by the presence of surfactants (S. Troian, Exxon).

Like films overlying a solid surface, 'free-standing' soap films, such as those that constitute bubble walls, attain a particular equilibrium thickness, but the



In the ternary mixture of water, oil and a surfactant, physicists interested in phase transitions have tapped an extraordinarily rich vein. The phase diagram abounds with phenomena inviting study: percolation, self-assembly, wetting and criticality to name a few. A surprisingly simple lattice model of the three-component system, proposed by Widom[11] and now extended by K. Dawson (Berkeley), can reproduce much of this behaviour, such as the percolation transition from oil-filled micelles to a bicontinuous oil/water phase interfaced by surfactant. To minimize the surface energy of the amphiphilic layer, the system can adopt periodic structures described by 'minimal surfaces' (S. T. Hyde, Australian National University). The classification and stability of these structures can be understood by borrowing concepts from topology.

Elsewhere in the phase diagram, surfactants may self-assemble into vesicles, lamellar phases or cylindrical micelles. These can be studied by rapid quenching of the solution, freezing the surfactant structures in a vitrified matrix which can then be probed by electron microscopy (Y. Talmon, Technion). An intriguing variant of the lamellar phase is obtained by incorporating small magnetic particles (around 10 nm in size), stabilized by coating them with amphiphiles (C. Quillet and P. Fabré, Collège de France). The lamellae of this 'ferrosmectic' phase can be realigned by an applied magnetic field. The figure shows a network of focal conic defects in the ferrosmectic phase viewed through a polarizing microscope. □

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dynamics of the thinning process involves qualitatively different physics. For a start, the total surface area does not change; and one must also account for the influence of the surfactant molecules (layers of which at the air–water interfaces stabilize the film in the first place). At low surfactant concentrations, the canonical theory of colloidal forces, DLVO theory[6], predicts two types of equilibrium film that differ in thickness: a common black film (10–100 nm) and a Newton black film (~5 nm). Mechanical disturbances can trigger thinning of the former to the latter.

When, however, the surfactant concentration is increased above the critical micelle point, the surfactant molecules aggregate into spherical micelles with their hydrophobic tails buried inside. The thinning process then occurs in a stepwise manner which can be observed as the nucleation and growth of dark (thinner) spots on the film surface[7,8] (P. A. Kralchevsky, University of Sofia). The steps are explained in terms of the packing of micelles, which adopt a layered configuration in films only a few micelle diameters in thickness. Calculations (C. J. Radke, University of California, Berkeley) show that the micelles can be regarded as essentially hard-sphere-like, a proposal supported by the fact that the same effect is observed in films containing a suspension of much larger latex spheres (Kralchevsky).

This stepwise thinning recalls the oscillatory force curves measured when a liquid such as water is compressed between two mica plates[6] (J. Israelachvili, University of California, Santa Barbara) — films only a few molecular diameters thick become stratified, and jumps in the inter-plate distance occur as successive layers are squeezed out. But the latter are equilibrium, first-order transitions, whereas the thinning of micellar soap films takes place spontaneously at constant pressure, each intermediate thickness being only metastable. The latter process is, in other words, a dynamical one.

The surface-force apparatus[9] described by Israelachvili can be said with justification to have revolutionized the measurement of short-range intermolecular forces. It is also now finding applications for dynamical studies. J. Klein (Weizmann Institute) reported on the effect of shear on the forces between two mica sheets coated with polymers (either grafted or adsorbed)[10]. By suspending the sheets on leaf springs, oscillatory tangential motion is possible, imposing a shear on the fluid between the plates. The lateral ('rubbing') force between the plates is affected remarkably little by shear, even at separations rather less than twice the effective length of the polymer chains. But the repulsive force normal to the plates increases when the shear velocity exceeds a critical value, whereas one might expect a decrease as the dangling chains get combed down. The polymer coats thus help to keep the plates apart under shear. It seems that adsorption of polymers has been given little consideration as a means of lubrication; but perhaps here the physics is for once telling chemical engineers something that empiricism previously has not. □

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POPULATION ECOLOGY

Chaos in time and space

Anthony R. Ives

ECOLOGISTS' hopes of explaining the population dynamics of plants and animals in terms of simple, stable interactions among species were shattered by the discovery in the mid 1970s that even simple interactions may result in chaotic population dynamics[1]. On page 255 of this issue[2], M. P. Hassell, H. Comins and R. M. May put to rest any such hopes that linger on — they show that simple interactions among species may lead not only to chaotic fluctuations through time, but also chaotic patterns in space where population booms and busts occur in a seemingly random pattern.

Morphogenesis

The idea that simple processes may lead to complex spatial patterns entered the field of biology in 1952. In his classic paper on morphogenesis, Alan Turing[3] demonstrated that simple chemical events can produce stable spatial patterns in chemical reactants. The minimum requirement is two chemicals, one an activator that stimulates the production of the second, which itself inhibits the first. Then, with certain diffusion rates, stationary wave-like patterns evolve in which ridges in the inhibitor concentration coincide with troughs in the activator concentration. This mathematical result has profound consequences for biological morphogenesis because it provides an explanation for pattern formation during the development of an initially homogeneous collection of cells, such as is found in an embryo.

Turing's model is closely akin to the ecological model considered by Hassell *et al.*, which addresses the interactions between a parasitoid and its host. (A parasitoid is a predator, typically an insect, which lays offspring in its host; the offspring then kill and consume the host.) Here, the activator is the host, and the inhibitor is the parasitoid. Both host and parasitoid diffuse throughout the environment which, for the sake of the mathematical calculations, is divided up into identical, contiguous patches. Thus this ecological model has all the ingredients needed to produce spatial pattern. The surprise that the spatial patterns are chaotic, however, comes from the type of interaction between parasitoids and hosts.

In Turing's model, the reaction between chemicals is stable; if the chemicals are confined to a small area so that diffusion is not an issue, the chemicals will reach stable concentrations. In Hassell *et al.*'s ecological model, the interaction between parasitoids and hosts is unstable; confining parasitoids and hosts to a small area will lead to the extinction of one or both. This is a natural assumption, because many experiments have shown instability in predator–prey interactions. With instability between the activator and the inhibitor, Turing's stable spatial patterns are replaced by a plethora of complex patterns, including spiral waves and true spatial chaos. Such exotic patterns seem to be the rule, with better behaved spatial patterns being the exception. Patterns like these are new to ecological models, because previous models assume (unrealistically, for most species) that hosts and parasitoids disperse evenly throughout a large region, rather than diffuse only among adjacent areas.

What is the evidence that chaotic spatial patterns exist in natural populations? The first place to look is controlled laboratory experiments that guarantee an initially homogeneous environment. For example, the patterns produced during Carl Huffaker's studies on the interactions between predatory and prey mites[4] look suspiciously like chaos. In his experiments, decreasing the freedom with which predatory mites could dis-

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