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Thin Film Mediated Phase Change Phenomena: Crystallization , Evaporation and Wetting

PI: Professor J.S. Wettaufer,
University of Washington, 1013 NE 40th Street, Seattle, Washington, 98105-6698

We focus on two distinct materials science problems that arise in two distinct microgravity environments: In space and *within* the space of a polymeric network. In the former environment, we consider a near eutectic alloy film in contact with its vapor which, when evaporating on earth, will experience compositionally induced buoyancy driven convection. The latter will significantly influence the morphology of the crystallized end member. In the absence of gravity, the morphology will be dominated by molecular diffusion and Marangoni driven viscous flow, and we study these phenomena theoretically and experimentally. The second microgravity environment exists in liquids, gels, and other soft materials where the small mass of individual molecules makes the effect of gravity negligible next to the relatively strong forces of intermolecular collisions. In such materials, an essential question concerns how to relate the molecular dynamics to the bulk rheological behavior. Here, we observe experimentally the diffusive motion of a single molecule in a single polymer filament, embedded within a polymer network and find anomalous diffusive behavior.

Alloy Films Here we consider the nature of crystallization of a two component volatile liquid in a film configuration. This geometry is important for several reasons. In the limit that the film itself is thinner than the capillary length on earth, the dominant effects influencing the equilibrium configuration are molecular diffusion, surface energy and long- and short-range intermolecular interactions. These are particularly crucial near contact lines. As the film builds in thickness, the role of gravity becomes important in both equilibrium and nonequilibrium configurations. By parity of reasoning, as a thick film thins, for example by evaporation, the influence of gravity wanes. Finally, as gravity itself vanishes we can extend the spatial range over which surface energy and long range interactions influence the behavior and we restrict our treatment of compositional evolution to diffusion and surface tension driven advection. We describe first the effect of evaporation in a pure film material and then examine the influence of a solute. From the perspective of the bulk coexistence, the evaporation of a completely wetting one-component fluid might be considered as the reversible conjugate of the wetting process. However, as was shown earlier in the research program, attractive interactions with the substrate eliminate the reversibility by stabilizing thin films against a subsaturated vapor phase, wherein the subsaturation controls the equilibrium film thickness. A nucleation process initiated by the tails of the long range substrate potential ruptures the thick film and leaves the substrate covered by a uniform thin film which is in coexistence with the subsaturated vapor, but the thin film is decorated by droplets of evaporating fluid. These droplets stand at finite (macroscopic) contact angle and hence evaporation of a pure fluid preempts the complete wetting of the substrate[1].

The addition of another component to the fluid introduces an additional thermodynamic constraint which dramatically changes the wettability and coating properties of the system. Experimental observations made on aqueous ammonium chloride[2] motivate investigation of a model system that exhibits some of the primary features of the observed morphology. Consider an incompletely wetting droplet of solution standing on a substrate at finite contact angle. The species dependent volatility of the fluid facilitates crystallization during evaporation. Crystallization appears near the contact line of the droplet which drives the material over the substrate, but with a highly ramified interfacial region near the contact line. This contrasts with the pure case wherein evaporation leads to the nonwetting of an otherwise wetting fluid. Hence, evaporation of a nonwetting alloy leads to wetting.

The process involves a host of effects not all of which can be accounted for simultaneously in simple scaling arguments much less in analytical treatments. Evaporation acts to enrich the solution and initiates solidification within. The interaction between this process, mass conservation, and the solutal Marangoni effect drives material from the interior of the droplet into the rim and over the substrate. In contrast to the vast majority of solidification systems driven by evaporation, the phase boundary moves away from the source material in a process we describe as "extended crystallization".

This complex interplay of phenomena motivates studies in which we can isolate dominant effects in idealized configurations. Common experience dictates that a bulk container of evaporating solution will eventually be populated by crystals. What is not intuitive is that the crystals will climb up the container walls. The observations require interpretation in terms of a continuous film covering the crystals near the contact line. As such, we first analyze the geometry of the solid/liquid interface underlying a semi-infinite thin film of solution. The structure observed is reminiscent of morphological instabilities, but because the source of impurities lies across the film, the front evolution is essentially different, akin to an activated instability.

We focus on a region of the crystal-film interface that is small relative to the characteristic variation in the vapor pressure. Hence, the solutal Marangoni flow that will arise in this system[3] will drive fluid into the region under consideration but the variation in surface tension over the scale of this region is small. The flow itself depends only on the coordinate normal to the solid/solution interface, $u(z) = \tau z / \mu$ where $\tau = d\gamma/dx = d\gamma/dC \, dC/dx$ is the Marangoni coefficient, wherein γ is the liquid/vapor surface tension and $C=C(x,z)$ is the solute concentration. The time independent evolution of the solute field in the film of thickness H is found by solving

$$\frac{\tau}{\mu} z \partial_x C = D \partial_{zz}^2 C \ , \qquad (1)$$

subject to $C(x,z=0) = C_E$ and $C(x,z=H) = C_O$ where C_E is the equilbrium interfacial concentration at the temperature of the substrate, C_O is the equilibrium concentration at the local vapor pressure of the liquid surface, and D is the solutal diffusivity. It is the variation in the vapor pressure along the surface that gives rise to the Marangoni flow and hence by allowing a weak variation in $H=H(x)$ we account for this effect. In so doing we find a similarity solution $C=\Delta C \, C(\eta)$ with similarity variable $\eta = z \, (D \, x)^{-1/3}$, in terms of ordinary functions

$$C(\eta) = \frac{\Gamma\left(\frac{1}{3}\right) - \Gamma\left[\frac{1}{3}, \frac{\eta^3}{9}\right]}{\Gamma\left(\frac{1}{3}\right) - \Gamma\left[\frac{1}{3}, \frac{\eta_H^3}{9}\right]}, \quad \text{where } D = \frac{\mu/\tau}{D\rho^2/Q_m^2} \text{ and } \eta_H = H \, (D \, x)^{-1/3}. \qquad (2)$$

The parameter D is a measure of the ratio of viscous to diffusive time scales, wherein ρ is the liquid density and Q_m is the mass flux at the liquid/vapor interface. It is fortunate that the physics of the problem suggests a spatially varying thickness because equation (1) is otherwise unseparable in a finite domain in z unless the problem is solved asympotically. Analysis of this solution shows that the flow provides material that maintains a constant film thickness in a spatial region Δx in which we would like to investigate the stability of the solid/liquid interface, but that this flow has a negligible effect on the redistribution of solute within Δx. From the perspective of the solid/liquid interface, the liquid/vapor interface is the source of solute. Hence, the solute introduced into the film at the liquid/vapor interface must diffuse through the film in order to advance the solid/liquid interface and, depending on the local temperature, any solute in excess of the local value of C_E will give rise to a local supersaturation. In the thin-film limit we have found a crystallization instability driven by this process[4]. In direct analogy with the frozen temperature approximation to the Mullins-Sekerka instability, the most dangerous mode is of zero wavenumber but the wavelength selection is weak, leaving us with the possibility of many modes manifesting themselves on the growth front. Hence, we have begun to understand why the observed contact line becomes so highly ramified.

As the initial value of the film thickness increases, two fluid mechanical phenomena become important and can therefore influence the evolution of the solidification front. The first is Marangoni flow given by equation (2) and in a zero gravity environment, this may influence the evolution of the interface by competing with the diffusive redistribution of solute. Because the flow has a large scale directionality, there is a possibility of travelling wave instabilities, for example, as has been found in directional solidification[5]. On Earth, as the film thickens compositional convection, driven by the increased density of the fluid near the solid/vapor interface, will begin. The critical conditions for the onset of compositional convection in 1 g are well described within the framework of the Oberbeck-Boussinesq equations. As gravity vanishes, the convective stability domain diverges. Therefore, we expect that in zero gravity, the film thickness alone will determine the relative importance of diffusion and Marangoni convection in influencing the nature of the solidification instability.

Molecular Motion *within* a Polymer Network

Another sort of microgravity environment exists in other soft materials such as polymer networks. The small mass of individual molecules makes the effect of gravity negligible next to the relatively strong forces of intermolecular collisions. A trivial example is that of a simple molecule in liquid solution. With a typical length scale L of 1 nm diameter and molecular weight 100, the gravitational force mgL is of order 10^{-33} N, while the thermally driven "Brownian" forces k_BT/L have the order of 10^{-12} N. Indeed this discrepancy is retained up to the scale of one micrometer, and Brownian motion plays a dominant role in the dynamics of colloidal suspensions.

The Brownian microgravity environment is characterized by unique mechanics. Battered randomly by molecular collisions, inertia is near zero and ballistic motion is impossible. Viscosity dominates so that force is proportional to velocity rather than acceleration. In the absence of bulk flows or other external forces, the motion of any single molecule or particle is diffusive, executing a random walk with mean square displacement growing linearly with time. The assumption of ideality rests on the claim that each molecule acts independently in a randomizing field of all other molecules. They do not develop significant correlations, and in bulk they are described by simple Newtonian viscosity.

In polymers and gels the nature of thermally driven motions is considerably more subtle. In addition to molecular translations, thermal energy may couple into many types of soft bulk modes. Undulations of membranes or polymer filaments are among the most important of these modes. The soft elasticity characteristic of rubbers, foams, and even many foods depends on these undulations. While these materials have a net bulk density, their internal dynamics are dominated by thermally driven fluctuations operating at any value of gravity.

Here, we take a direct look at the diffusive motion of a single molecule in a single polymer filament, embedded within a polymer network. Of course it is impossible to image and trace in time the motion of an individual molecule. Most work concerning such topics relies on spatial-averaging methods such as light scattering. Molecular motions are inferred from observations of density fluctuations.

Our approach is to tag a point on a polymer with an optically resolvable microsphere (silica bead, 0.3 μm diameter), whose motion we follow with microscopy and video analysis tools. In order to reach observable time and length scales, we exploit particular biological polymers called microtubules. These are semi-crystalline polymers of the protein tubulin, which spontaneously forms hollow tube structures 25 nm in diameter and up to hundreds of micrometers in length. In vivo, these are ubiquitous structures present in the cells of animals and plants. For our purposes, their large diameter gives them a rigidity in the optimal range for optical measurements: they are sufficiently rigid to maintain an average direction from end to end, but still flexible enough to bend and undulate under the influence of thermal motion. (Thermal energy is distributed by equipartition into bending modes, each one costing curvature energy proportional to the fourth power of its wavenumber.) In other words, the motion of the bead should reflect the undulation of the whole polymer, in contrast to the free translational diffusion it would normally make in solution.

Experimental methods include the biochemical purification of tubulin from cow brain, development of a chemical surface treatment by which to attach beads to microtubules (in preference to free tubulin in solution), differential interference contrast microscopy, optical tweezers for manipulating the tiny beads and for verifying their proper attachment, and development of particle-tracking software for video analysis. The measurements were always of the bead position as a function of time. These were accumulated into charts of mean squared displacement vs time interval, on intervals ranging from the video rate of 25 frames per second to several seconds.

The main results are interpreted as follows[6]. At "short" times, the motion of the microtubule undulations generates a mean squared displacement which grows as $t^{3/4}$, in contrast to t^{1} for ordinary translational diffusion. At "long" times, the mean squared displacement reaches a saturation. Both the saturation amplitude and the crossover time between short and long regimes depend on the density of the polymer network. Essentially, the crossing, or "entanglement" of one filament over the next limits the undulations, dividing the polymers into segments shorter than the physical length and constraining the free oscillation of the longest wavelength modes. As a control, a bead attached to a microtubule which is not entangled in a network shows only ordinary linear diffusion on the observable time scales. An unexpected experimental result was obtained when observing a sheared network of microtubules. The beads displayed a mean squared displacement growing as $t^{1/2}$, which is interpreted as a signature of tension in the polymer filaments to which they attached. In this case thermal energy is distributed into bending modes costing energy proportional to the square of the wavenumber.

Future Outlook Our study of the alloy films will focus on two areas. Firstly, we will investigate the role of the local shear rate in the evolution of the morphological instability. We expect that for sufficiently rapid flow, the disturbance maxima will experience a different supersaturation depending on whether they are upstream or downstream of the flow. Secondly, we would like to apply more simplified models to the droplet configuration. It is possible that one can explain the essential aspects of the spreading without having to treat the complex dynamics at the contact line. Finally, we would like to begin studying the role of long-ranged intermolecular interactions on the evolution of the surface film.

The study of polymeric networks will proceed by installation of a fast position-sensitive detector to eliminate the video-rate restriction, and introduction of a probe to the local-scale rheology of the system. We are constructing a microscope-based falling-ball viscosimeter using a bead which is heavy enough to sediment by gravity through networks of microtubules of various mesh densities. We will use the system to investigate the fluctuations in the falling bead's decent as a signal to its interaction with the network. We will then move to a network of microtubules crosslinked by smaller adhering beads, again focusing on the local-scale rheology seen by the individual particle.

References

[1] M. Elbaum & S.G. Lipson, *Phys. Rev. Lett.* **72** 3562-5 (1994); M. Elbaum, S.G. Lipson, & J.S. Wettlaufer, *Europhys. Lett.* **29**, 457-62 (1995); *ibid*, **39**, 342-4 (1997).

[2] R. Du & H.A. Stone, *Phys. Rev. E* **53**, 1994-7 (1996).

[3] S.A. Lowry et al., *J. Cryst. Growth* **96**, 774-6 (1989).

[4] J.S. Wettlaufer & H.A. Stone, *Bull. Am. Phys. Soc.*, **41** 1723 (1996); J.S. Wettlaufer, M. Elbaum, H.A. Stone & M.G. Worster, *Proc. NASA Microgravity Materials Sci. Conf.* NASA/CP-1999-209092, p. 679-83.

[5] Forth & A.A. Wheeler, *J. Fluid Mech.* **202**, 339-66 (1989).

[6] A. Caspi, M. Elbaum, R. Granek, A. Lachish & D. Zbaida, *Phys. Rev. Lett.* **80**, 1106-9 (1998); *Bull. Am. Phys. Soc.*, **43** E13 .14 (1998).