Between two and three dimensions

The physics of molecular films evolves from two dimensional to three dimensional as the films thicken, but remnants of two-dimensional behavior persist in bulk materials.

J. G. Dash

One of the most glamorous aspects of monolayer films is their thinness, and another is their two dimensionality. These properties are not the same, of course, although it might seem that each implies the other. We know some monolayers that are not two dimensional, and some much thicker films that are nearly so. Even more confusing is that a film can be two dimensional and three dimensional—and somewhere in between—at the same time. A simple change of temperature can change a film's dimensionality.

What we mean here by dimensionality and how we measure it are the topics of this article. I will try to explain by drawing on some recent results from a rich and active field of research.

The field is a relatively new branch of condensed-matter physics. It had its modern beginnings about 15 years ago, with the development of materials and experimental techniques for studying monolayer films on uniform surfaces. Since then it has attracted the interest of many theorists and experimenters throughout the world, who have contributed greatly to "lower-dimensional physics." Their fundamental studies have significant practical implications for several areas of materials science, such as adhesion, lubrication, fracture, anticorrosion coatings and the production of integrated circuits. A recent seminar on wetting and growth held at Brookhaven National Laboratory with joint support by the National Science Foundation and the French Centre National de la Recherche Scientifique, brought together some 45 scientists who do fundamental and applied research in the field.

Stepping down to two dimensions

Let us start with a *gedanken* experiment. In an imaginary three-dimensional container we explore the ordinary bulk phases of a simple substance. To be specific, let us choose xenon and make the container a cube large enough to hold one mole of the element at its critical point. Manipulating temperature and pressure, we find the familiar solid, liquid and gas phases of ordinary matter; we get the familiar phase diagram, figure 2a, showing the domains of the three common phases.

Now, let us begin to remove the material gradually, with the temperature set somewhat below the triple point. The pressure remains constant for a long time, until all but a few millionths of the original quantity is removed. At this point we find the pressure dropping, first almost imperceptibly, then more rapidly. If we have taken some pains in constructing the container, namely, if we have made the inside walls of basal-plane graphite, the isotherm begins to show a series of steps, as in figure 3, each step associated with the removal of a single molecular layer:[1] Think of it as a staircase down to two-dimensional physics.

Finally, with quantities of material no greater than a micromole remaining, we examine the phases of the last layer. We are amazed—or we *should* be amazed—to find a phase diagram (figure 2b) remarkably similar to the bulk diagram (figure 2a). It has the same architecture, although it is only a shadow of its former self. Here are distinct regimes, occupying about the same regions of the phase diagram where the corresponding three-dimensional phases—solids, liquids and gases—lie.[2,3] Of course, we must measure various properties in each region to know whether or not the phases are in fact solid, liquid or gaseous. We make measurements of all kinds, using the same types of probes used to explore the bulk. We find that these phases do indeed resemble bulk solid, liquid and gas states, but with important differences. In a two-dimensional liquid, for example, there is no long-range order, and atoms can diffuse along the surface but are bound in the normal direction. We explore these differences below, but for the moment we just inspect the two

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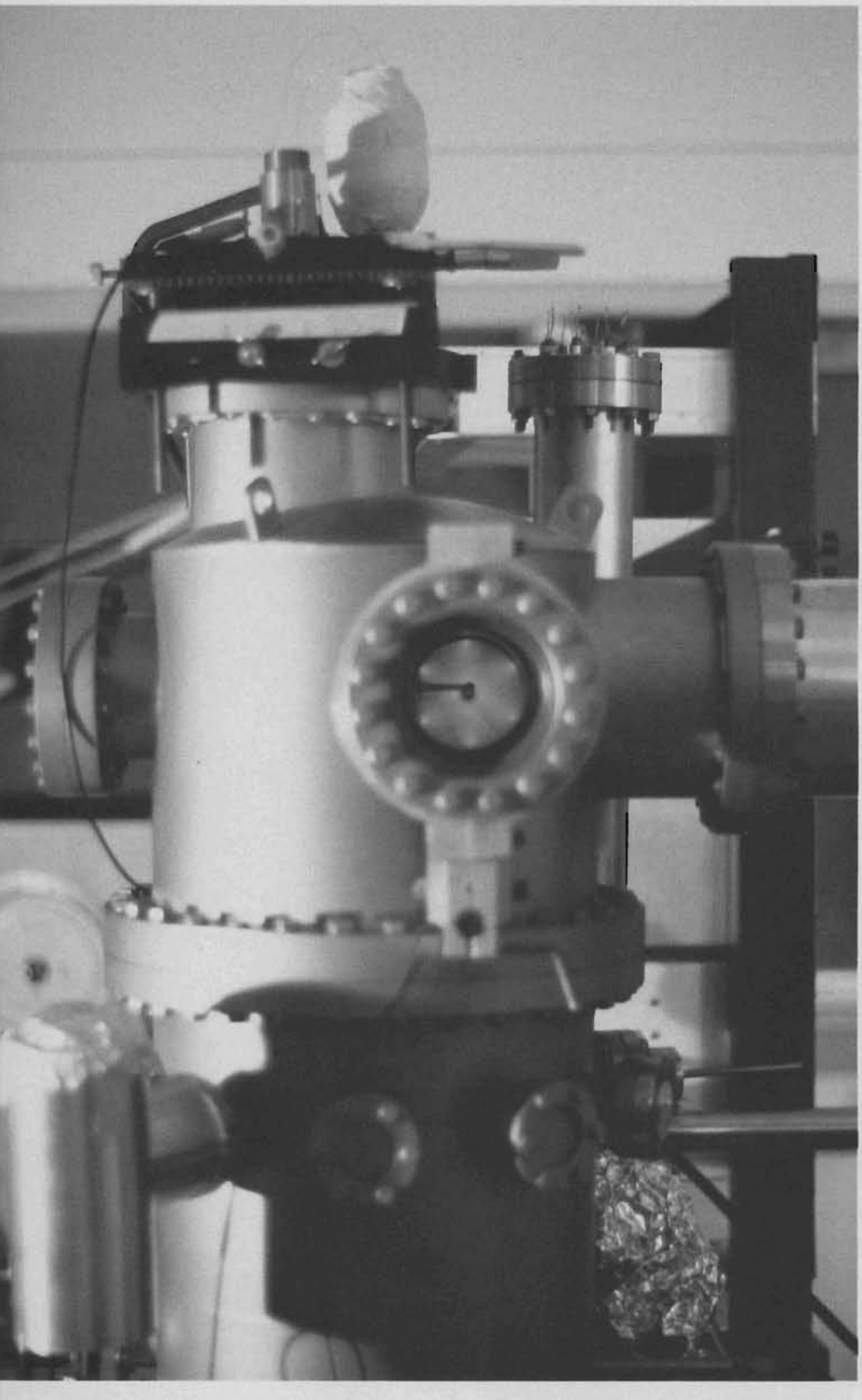


Apparatus used to study the two-dimensional structures and phase transitions of monolayer films adsorbed on single crystals. Electron diffraction from the surface of a graphite crystal is visible in the photograph. This low-energy electron diffraction apparatus was built at the University of Washington by Martin Chinn and Samuel Fain. Figure 1

diagrams. We see that the critical and triple-point temperatures $T_c(2D)$ and $T_t(2D)$ of the monolayer are substantially lower than those in the bulk. Quite generally, for all simple substances on all known uniform substrates,

$$T_c(2D)/T_c(3D) \approx 0.4$$
$$T_t(2D)/T_t(3D) \approx 0.6$$

One can understand these ratios simply as a result of the reduction in coordination number in the monolayer: Each atom has fewer neighbors with which to interact, a very direct consequence of reduced dimensionality. Let us examine some of the phases and transitions in more detail.

Phases in two dimensions

The first systems to show clear two-dimensional gas-like features were semisoluble oil-on-water films, in studies that began[4] in the 19th Century and continue to this day. The crucial, identifying property is the spreading pressure ϕ, which can be measured directly by the force on a sliding surface barrier.

The sliding barrier device will not work for monolayers adsorbed on solid substrates, but instead one can measure the spreading pressure ϕ by its effect on the substrate: The monolayer causes a very small dilation of the substrate's surface area. One can also measure the two-dimensional pressure indirectly, through its thermodynamic connection with the vapor pressure of the film. For either type of measurement the relation between the spreading pressure ϕ and the surface density n is the equation of state of the monolayer:

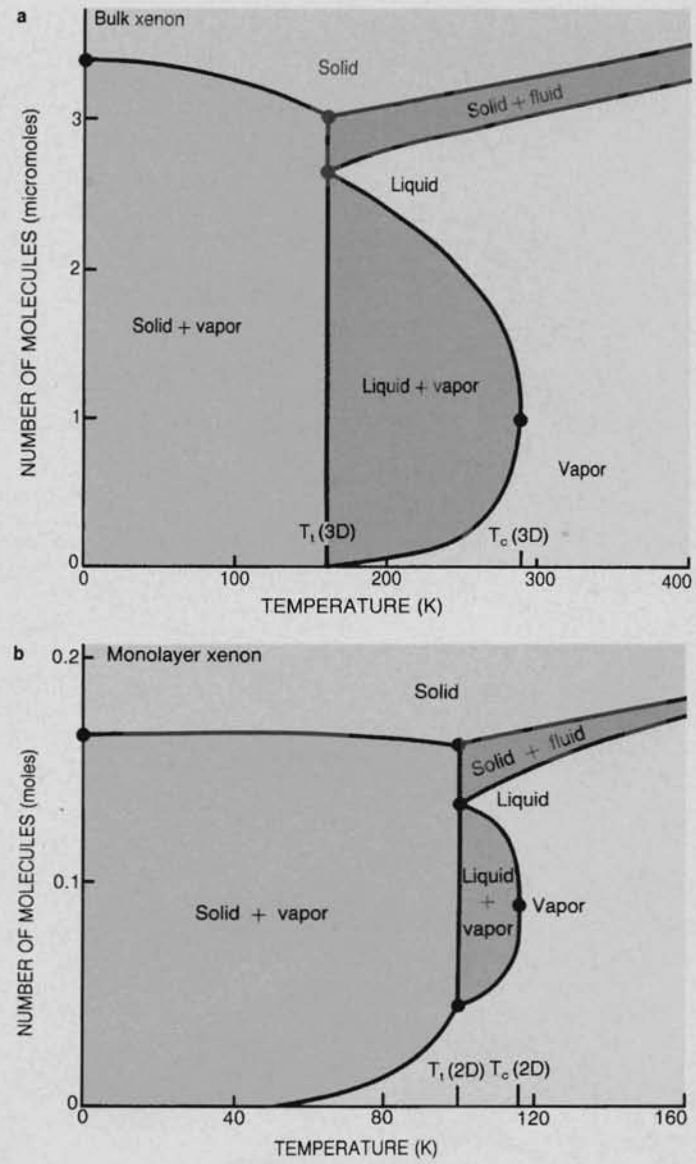
$$\phi = nkT(1 + nB)$$

This equation contains a correction to the ideal-gas relation due to interactions between pairs of molecules. The factor B in this term is the two-dimensional second virial coefficient of the film. Heat capacity C is another property with a highly distinctive signature. With the virial correction, it is given by

$$C = Nk\left[1 - \frac{n}{(kT)^2}\,\frac{d^2B}{d(1/kT)^2}\right]$$

Both kinds of measurements have

Phase diagrams for three-dimensional xenon (**a**) and monolayer xenon (**b**). The vertical scale in **a** is computed for a cubical vessel that can contain one mole of xenon at its critical point. The vertical axis in **b** measures quantities adsorbed on the (graphite) walls of the same container.[2] Figure 2



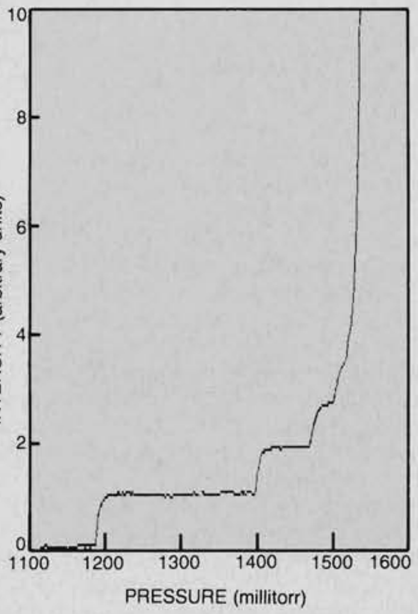
given clear two-dimensional signatures for several types of monolayer systems: He^3 on liquid He^4 (reference 5), He^3 and He^4 on bare and rare-gas-plated graphite (reference 6) and hydrocarbons on graphite (reference 7). What is particularly convincing is that the experimental virial coefficients are in some cases extremely close to those from first-principles calculations.[8] Recently the theory and the measurements have become so precise that strictly smooth-substrate approximations are not always adequate: One can measure effects due to the atomic structure of the substrate, which takes the form of a corrugated surface.[9] That seems to bring us back to the real, three-dimensional world, destroying our concept of the films as two dimensional. However, we can continue to treat the film as two dimensional by incorporating the effects of the third dimension into the equations that describe the film. Corrugations tend to discretize the space into a two-dimensional lattice of adsorption sites, so that the monolayer becomes a two-dimensional "lattice gas." If the atoms move rapidly between sites, we can describe their motions in terms of a two-dimensional band model, analogous to the conventional treatment of electron mobility in a three-dimensional metal or semiconductor.

There are many effects that can compromise the two dimensionality of monolayer films. As the box on page 32 indicates, the list is fairly long. While this might tend to discourage the timid, it also presents a challenge. One can modify two-dimensional models to include some of the effects, but there are limitations, which will come up a little later. For now, we continue to examine a few effectively two-dimensional models and their experimental confirmations.

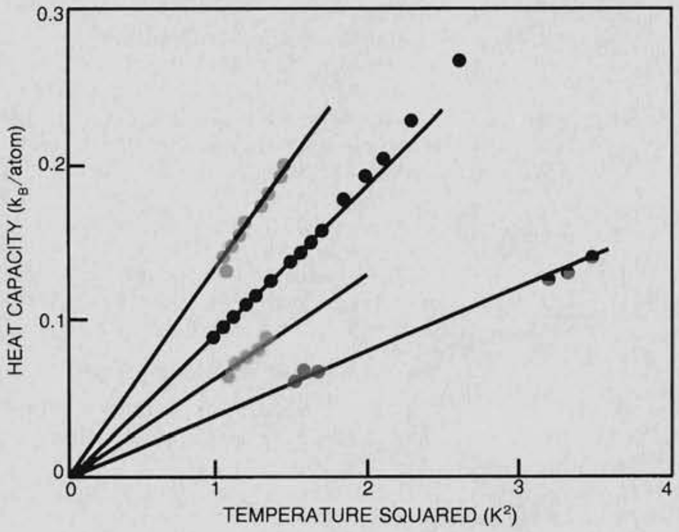
There are two basic classes of solid monolayers: those in which the atoms are localized in a regular structure determined by the substrate, and those, sometimes called "floating" solids, that are incommensurate with the substrate. Both types have distinctive structural, dynamic and thermal properties that appear in a number of adsorption systems. The microscopic signatures of both classes of solids are crystallinity, long-lived vibrational modes and anisotropic spectra. Measurements based on neutron, electron and x-ray diffraction, inelastic neutron scattering, nuclear magnetic resonance and Mössbauer spectroscopy have revealed these characteristics.[3,10–12] The thermodynamic characteristics of solid monolayers are particularly distinctive at low temperatures. For example, the heat capacity C of a floating solid follows a simple power law in temperature: $C \propto T^2$. This quadratic dependence contrasts with the T^3 law of a three-dimensional solid. The exponent is equal to the dimensionality of the system.

Quadratic heat capacities were the first clear indication of two-dimensional behavior in adsorbed monolayers. David Goodstein of Caltech found[13] these T^2 heat capacities some 20 years ago in a study of helium on copper sponge. It was the failure to find the expected liquid and gas phases at lower densities that led to the understanding that the solid-like behavior was largely due to compression of the monolayer by the heterogeneous substrate fields. That stimulated a search for more uniform surfaces, leading researchers to Union Carbide's Grafoil and other forms of crystalline graphite, substrates that have been the mainstay of most of the experimental work in the field. Figure 4 shows the results of a more recent series of measurements[14] that clearly show two-dimensional solid character.

The temperature and density signatures of the liquid phase are much less distinctive, and are not markedly dependent on dimensionality. One can



Layer-by-layer growth of krypton adsorbed on crystalline graphite at 78 K. The measurements were made by optical ellipsometry at the University of Virginia by Mahrez Drir, Hyun Soo Nham and George Hess. Xenon displays similar steps, but available data are less detailed.[1] Figure 3



Heat capacities of solid monolayers of He^4 adsorbed on graphite at several surface densities, measured by Suzanne Hering and Oscar Vilches at the University of Washington. The plot against the square of the absolute temperature shows the quadratic dependence characteristic of two-dimensional solids.[14] Figure 4

also deduce liquid phases from gross features of the phase diagram—the densities and locations of phases in the overall diagram in those regions where liquid coexists with two-dimensional vapor. The most convincing indications that the liquids are *two dimensional* have come from the shape of the liquid–vapor phase boundary near the critical point.

The liquid–vapor boundary in figure 2b is extremely blunt, which is a distinct characteristic of two-dimensional behavior. Theory predicts this profile, and experiments have found it in several monolayer systems. In figure 5 we compare two experimental measurements, one on a bulk substance[15] and the other on a monolayer film.[16] The measurements are of different gases, but from the same laboratory. In bulk neon, the density difference between liquid and vapor along the boundary near the critical temperature is described by a power law:

$$(n_{\mathrm{liq}} - n_{\mathrm{vap}}) \propto (T_{\mathrm{c}} - T)^{\beta}$$

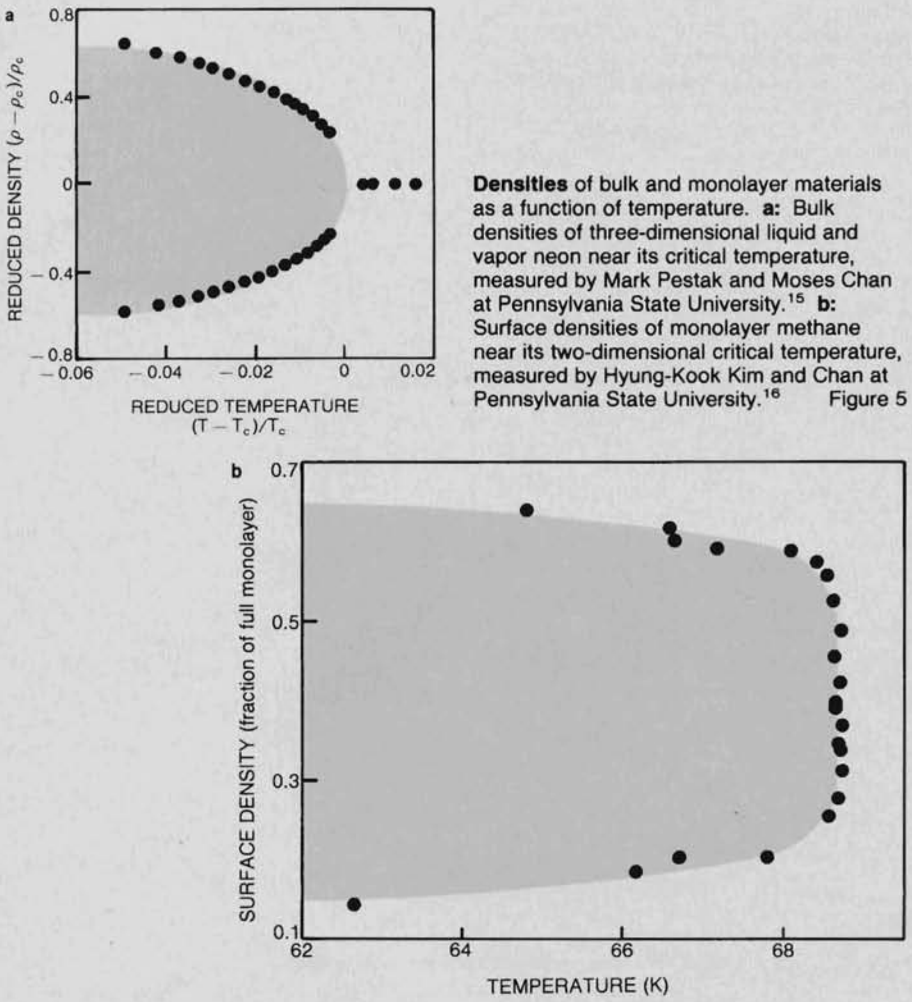
The experimental critical exponent β is 0.32, close to the theoretical value of 0.325.

The surface density of a two-dimensional system at the liquid–vapor boundary also varies as a power law, but the critical exponent is different. The experimental value for the methane monolayer is 0.13, nearly equal to the theoretical $1/8$ for a two-dimensional system. Yet does this correspondence show that the film is entirely two dimensional? *No.* Some properties may be rather bulk-like even in the midst of the two-dimensional critical region. Molecular excitations, for example, are appreciable in the direction normal to the surface. Vibration amplitudes and frequencies may well be anisotropic, but fully excited in all directions. It is the phase transition between the thin liquid film and the vapor that is two dimensional. Moreover, the transition itself is imperfect due to three-dimensional effects in which the finite sizes of surface domains and variations in substrate attraction blur the transition very close to the critical temperature. Hence we must be satisfied with a partial signature: The exponent agrees with the two-dimensional model over a pretty wide range of temperature.

Climbing back toward 3D

After these few examples of behavior that is clearly two dimensional, we turn to the question of dimensionality *per se*. The examples illustrate that it is possible to put descriptions within two-dimensional theoretical frameworks, even when strict two dimensionality is seriously compromised. But then, can one always force the picture, or are there regimes where the physics of the system demands one or the other, or intermediate dimensionality? If we add a second layer and higher layers, how does a film evolve to bulk?

To inspect condensation further, let us consider a film of several layers. Interactions between layers lower the free energy, and tend to increase the critical temperature, so that as the



Densities of bulk and monolayer materials as a function of temperature. **a:** Bulk densities of three-dimensional liquid and vapor neon near its critical temperature, measured by Mark Pestak and Moses Chan at Pennsylvania State University.[15] **b:** Surface densities of monolayer methane near its two-dimensional critical temperature, measured by Hyung-Kook Kim and Chan at Pennsylvania State University.[16] Figure 5

thickness L becomes large the critical temperature $T_c(L)$ approaches the bulk critical temperature $T_c(3D)$. If we take the critical temperature as the gauge of dimensionality, we conclude that the film gradually evolves with the thickness L, from two dimensionality to three dimensionality.

However, there also are other criteria for dimensionality. Near the critical temperature T_c the properties of a substance are markedly affected by fluctuations of density, energy and other thermodynamic quantities. As the temperature is raised toward the critical temperature, the fluctuations become slower and extend over larger distances. The typical distance—the coherence length ξ—varies with temperature according to the equation

$$\xi \propto (T_c - T)^{-\nu}$$

The exponent ν for condensation in three dimensions is calculated to be 0.63. Far from the critical temperature T_c, the coherence length ξ is small. If the coherence length is much smaller than the thickness L the effects of the finite thickness are unimportant, and hence the film resembles bulk material. However, as the temperature approaches the critical temperature, the coherence length grows until it becomes comparable to the thickness, so that the fluctuations become truncated in the direction normal to the plane of the film and begin to lose their transverse degree of freedom. The process continues, and the condensation becomes effectively two dimensional. The crossover between the two regimes is gradual, occurring around the temperature

$$T \simeq T_c(L)[1-(a/L)^{1/\nu}]$$

Here a is the thickness of one layer. Therefore, far from the critical temperature the phase boundary curve has the same shape as the curve for bulk material, but approaching the critical temperature it changes gradually to the much blunter shape of the phase boundary curve for two-dimensional material. Physicists have discussed[17] this effect in the context of superfluidity and superconductivity. As of yet there has been no experimental search for the effect in multilayer condensation, although it should be experimentally accessible in adsorbed films.

There are other domains in adsorbed films that may show the transition between two dimensionality and three dimensionality, but the criteria are different. In solid multilayers, for example, we expect a changeover between T^2 and T^3 heat capacities as we vary the temperature. The heat capacity at any temperature is due primarily to the dominant vibrational modes, whose frequencies are approximately $kT/\hbar$. If the thickness of the film is much greater than the wavelength corresponding to this frequency, the boundaries have little effect, and the system is nearly three dimensional. However, as the temperature decreases, the dominant wavelength increases, until the wavelength becomes comparable with the thickness L. At lower temperatures, vibrations normal to the plane of the film become difficult to excite, and only those in the plane of the film remain thermally excited; the exponent of the temperature in the expression for the heat capacity changes from 3 to 2. The temperature at which the solid heat capacity shows the dimensionality transition depends on the velocity V_s of the vibrational waves:

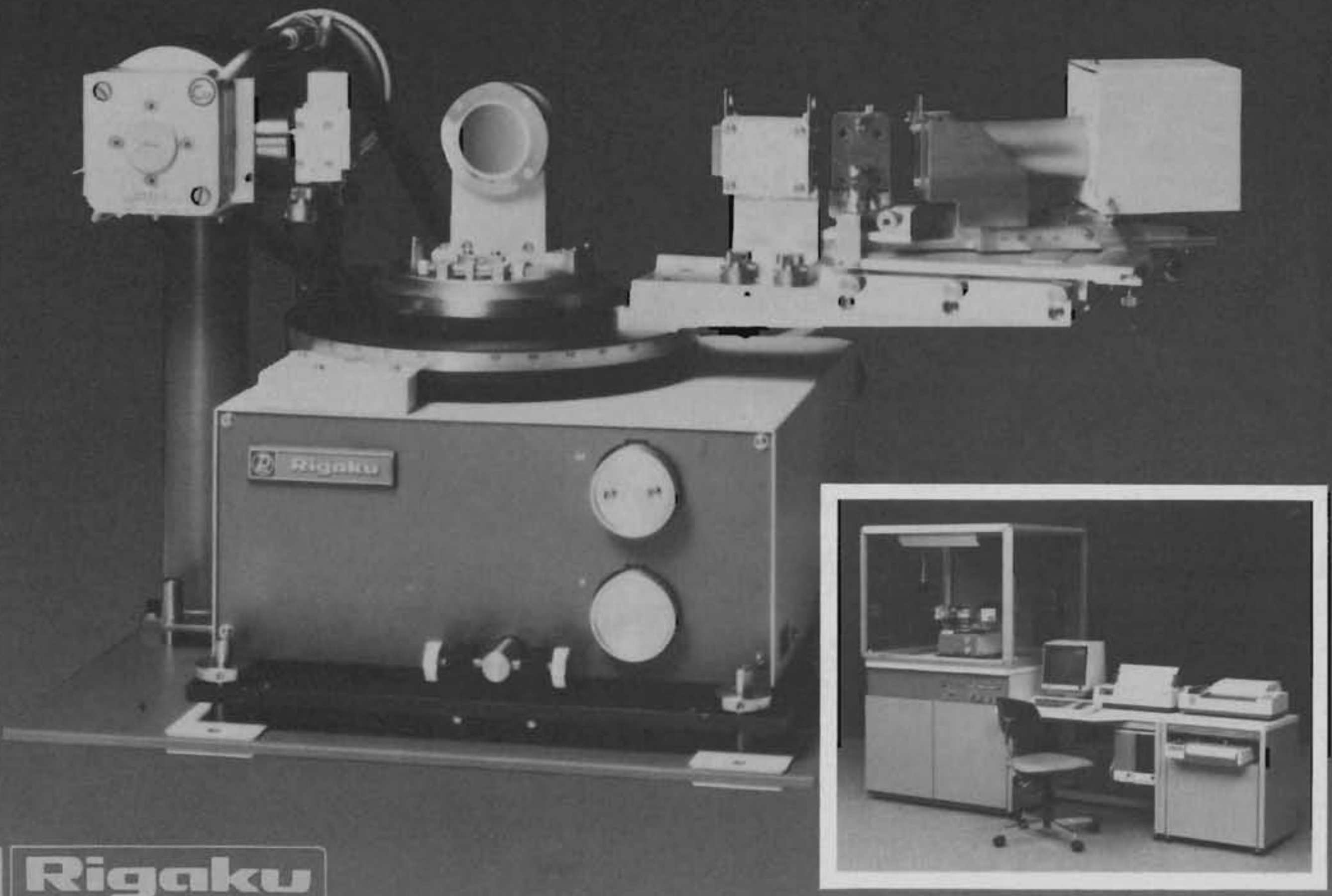
$$T \simeq 2\pi\hbar\, V_s/kL$$

These examples show that the gauge of dimensionality is specific to the property and temperature in question.

Transitions between dimensions

Now we have quite definite predictions, and we would like to put them to experimental tests. For that, we must prepare a series of films of uniform thicknesses varying from a few layers to perhaps several hundred. Unfortunately, we find that it is not generally possible to make *stable* films of arbitrary thickness. For some atom–substrate combinations, there is practically no adsorption whatsoever: If one deposits a small amount of material on the surface, the atoms condense into a bulk liquid droplet or, if the temperature is low enough, a bulk crystallite. Familiar examples are mercury on glass and water on wax. This "nonwetting" occurs when adhesion to the substrate is weak compared to the cohesive forces in the droplet.[18] In these systems two-dimensional phases do not exist.

For other combinations of atoms and substrate, wetting may be "incomplete." With these systems one can plate a small number of solid layers at low temperature, but further deposits cannot increase the thickness uniformly; they rather produce one or a few bulk crystals on top of the film. The dimensionality passes abruptly from 2 to 3. Such films evidently result from strains induced by fields from the substrate, which make the thin film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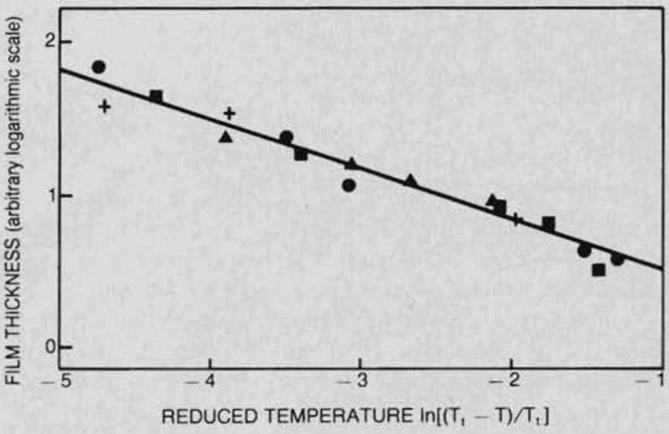

Maximum film thickness. The thickest uniform film that a substrate will adsorb depends on the temperature. This plot is for xenon (circles), krypton (squares), argon (crosses) and molecular nitrogen (triangles) on gold and silver substrates near the triple-point temperatures T_t of the bulk materials. The slope of the log–log plot is $-\frac{1}{3}$; this exponent of the power-law dependence arises from variation of the range of the substrate potential. The thicknesses were determined by Jacqueline Krim, Jean Suzanne and the author at the University of Washington by measuring the changes in resonance of a quartz crystal.[21] Figure 6

incommensurate with the surface planes of the bulk solid.[19,20] Only in films that have exactly the same lattice structure as bulk planes can one add layers *ad infinitum*. And that can occur, one expects, only on a substrate with a structure and adhesive force identical to those of the bulk itself.

Fortunately, there are exceptions. When one warms an incompletely wet solid film at low pressure to a temperature close to the triple point of the bulk, T_t(3D), the top layer melts. Now there can be no lattice mismatch between this top layer and the bulk planes, and one can add a number of further layers by increasing the pressure. But if the temperature remains below T_t(3D), only a limited number of layers can be added: At some finite thickness, the original top layer and the new layers above it solidify, so that there is bulk crystallization of a thicker film.

This process continues, we think, all the way to the triple point. The phenomenon is called "triple-point wetting." Figure 6 shows results from a recent study[21] of the effect. Experiments in the future may make use of the effect to grow stable films of large thickness, and thereby to explore the gradual evolution to bulk behavior.

Life between 2D and 3D

Triple-point wetting is closely related to a phenomenon thought to occur in bulk solids: surface melting.[22] Theory indicates that the surface of a solid crystal begins to melt, layer by layer, well below its normal melting point, although experimental confirmations are not yet completely convincing. We expect that the thickness of the liquid surface film grows gradually as the temperature rises, finally becoming infinite at the triple point. The intrinsic first-order melting of a bulk crystal infinitely far from its boundaries is surely abrupt, but that can occur only in an infinitely large crystal. For large but finite crystals, the melting transition may experimentally appear to be discontinuous, but it is in principle smooth. Because all real crystals are finite, they all have boundaries, which introduce aspects of two-dimensional physics into their actual behavior.

We began by exploring two-dimensional physics in some exotic systems, theoretically attractive but until recently difficult to create. We end by finding two-dimensional physics in the bulk materials of ordinary experience.

In the real world we are wrapped by surfaces, and therefore we live between two and three dimensions.

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Three-dimensional effects

These effects can compromise the two-dimensionality of monolayer films:

Substrate structure
- Localization on adsorption sites
- Mobility bands
- Commensurate film structures

Surface-normal excitations
- Atomic vibrations
- Multilayer occupation
- Vapor exchange

Substrate distortion
- Induced dipole shielding
- Elastic dilation and compression
- Mattress effect

Substrate imperfection
- Orientational disorder
- Finite-size effects
- Binding-energy heterogeneity