three-dimensional crystals that tend to melt from the surface inward (4). The colloidal crystals slowly evaporate down to a critical size and then “explode” to form a dense amorphous phase. This phase is unstable and subsequently evaporates.

Why would a small colloidal crystal suddenly convert into an amorphous phase that is thermodynamically unstable? The answer may be contained in a paper published almost 40 years ago (5). There, Cahn explained how metastable phases can act as crucial intermediates during the transformation from an unstable to a stable phase. In the present experiments, the intermediate phase is the dense liquid that, for colloids with short-range attraction, is not thermodynamically stable. Evans and colleagues (6) have reported experimental evidence for the Cahn scenario in colloidal systems with a somewhat longer-range attraction.

Savage et al. do not show direct evidence for the solid-solid transition expected for systems with short-range attraction. But they show something else: As the sublimating crystals get smaller, their density decreases. This seems strange, because small liquid droplets tend to be more compressed than larger droplets as a result of the surface tension. However, the observed expansion of small crystallites agrees well with simulations (7), which predict such an effect in the vicinity of a metastable solid-solid critical point (see the first figure, panel C). Hence, although the solid-solid critical point in colloids has not yet been observed directly, it seems to be within reach. To observe it, the size distribution of the colloids would have to be narrower (see the first figure, panel D).

Many proteins have short-range attractions similar to those of the colloids, but their clustering and dissolution cannot be studied directly by videomicroscopy. Hopefully, microscopy studies of colloidal model systems such as those studied by Savage et al. will provide insights into the kinetics of phase transformations in these important biological processes.

References

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PHYSICS

Beyond the Particle in the Box

Lars Walldén

Metal films and metal-semiconductor junctions are key components in modern electronic devices. On page 804 of this issue, Speer et al. (1) examine the energies of electrons in perfectly smooth and ultrathin silver films on silicon substrates. As expected, the authors observe energies that reflect the wave nature of electrons confined to a thin film. However, they also detect energies characteristic of a new type of electron wave. The latter extends through the film and into the substrate to a depth determined by the doping level of the substrate (see the figure). This observation has important implications regarding the basic physics of metal-semiconductor systems, especially those in which the film and the substrate have crystal lattices that do not match.

The principles of quantum mechanics are usually introduced to students through the example of the particle in a box. In this example, a particle (such as an electron) is placed in a confining structure. The rules of quantum mechanics then specify the allowed states of the particle. An excellent example of particle-in-a-box (or quantum-well) behavior involves valence electrons in thin metal films. If the film is a simple metal such as aluminum, an alkali metal, or a noble metal, the electrons can essentially be regarded as free particles (but they are prevented from leaving the solid by a potential barrier at the surface). This confinement perpendicular to the surface leads to a set of standing waves, allowing only specific wavelengths to exist. In the parallel direction, there is no similar restriction on wavelength. The electronic structure is thus characterized by a series of electron energy bands, one for each wavelength allowed by the confinement.

The discrete character of the bands leads to film thickness–dependent properties (2). For example, the cohesive energy and the work function can show an oscillatory thickness dependence of substantial amplitude. These oscillations occur because, as the film thickness increases, the quantum-well states shift to lower energies to accommodate more electrons. At regular thickness intervals, new states become populated, such that the balance between electrons with high and low energy varies periodically with thickness. In experiments, the thickness is not a continuous variable but varies in steps given by the thickness of an atomic layer. If the period is incommen-

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A matter of doping. Photons eject electrons from silver films deposited on silicon substrates, thereby yielding information about the electronic structure of the system. (Left) A single electronic level (or quantum-well state) is confined by the band gap of a lightly doped n-type silicon substrate. (Right) For a heavily doped n-type silicon substrate, the band edge of silicon varies near the interface, giving rise to additional quantum-well states that coherently span the silver film and a portion of the silicon substrate. In both cases, each quantum-well state (purple lines) exhibits a parabolic dispersion as a function of the in-plane momentum $k_x$. The author is in the Department of Applied Physics, Chalmers, 41296 Göteborg, Sweden. E-mail: wallden@fy.chalmers.se

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surate with the layer thickness, one is left with a beat period. This beat period appears in transport properties such as magnetoresistance (3).

The discrete electronic structure of a thin metal film was first observed experimentally via the tunnel current across a metal-insulator thin-film sandwich (4). Because the film served as an electrode, it had to be conducting, which meant that the thickness had to be at least \(~10\) nm. Later work demonstrated that photoelectron (5, 6) and scanning tunneling spectroscopies (7) are powerful tools to probe the electron states in thin adsorbed films down to monolayer thicknesses.

When the adsorbed film is only few atomic layers thick, the boundary conditions are particularly important. If a film is taken from vacuum and placed on a substrate, then it matters what the substrate is. Within a substrate energy gap (an energy range in which no valence electrons are found and which is often referred to as “forbidden”), one may find discrete quantum well–like states in the film. These states extend into the substrate, but only with an oscillating tail, with the period given by the substrate lattice. The decay depth of the state is given by the energy of the state with respect to the edges of the energy gap, the tails being long near the edges. The electronic state is thus a hybrid with a distinctly different character in the film and in the substrate.

Speer et al. have now used photoemission spectroscopy to study quantum-well states in silver films deposited on silicon. The silver films are 8 to 12 atomic layers thick. At these thicknesses, one would not expect the choice of substrate to be important for the ladder of energy bands. For example, nearly the same quantum-well state energies are observed when silver films are adsorbed on gold (8) as on the silicon substrate used by Speer et al. But as Speer et al. show, a dramatically different set of states can be obtained by increasing the doping of the silicon substrate.

When the Ag film and n-type Si are brought in contact, equilibrium (coincident Fermi levels) requires a transfer of electrons from Si to the metal. Near the interface, the semiconductor is depleted of electrons and the electron states are shifted in energy with respect to the states in the bulk. The depth dependence of the energy is referred to as band bending (9). With high n-doping (see the figure, right), the band bending saturates at a depth that is shallow enough for a novel set of discrete states to form. The electrons that form these states encounter the confining substrate band gap within the substrate and not at the interface. This means that the quantum well becomes wide, ranging from the vacuum interface to the depth where the energy coincides with the lower edge of the gap. The states therefore become less separated in energy than the standard type of quantum-well states.

The results reported by Speer et al. provide a detailed image of the electronic structure at a metal-semiconductor junction. The authors can account for their observations with simple models that can easily be extended to overlayers with different thickness and to substrates with different impurity content, or where the band bending may be changed by illuminating the interface (10).

Given the long and troublesome history of accounting for the properties of metal-semiconductor junctions (11), it is encouraging that there are cases in which simple modeling does not appear to be hampered by the occurrence of defects, intermixing, or compound formation at the interface. Furthermore, the effects reported by Speer et al. could be used to systematically modify the quantized electronic structure of thin film systems, thereby providing a powerful means for tuning properties of interest.

**References**


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**ECOLOGY**

### A Renaissance in the Study of Abundance

**Brian J. McGill**

Ecologists have borrowed a powerful tool from physics to calculate how environmental constraints affect the abundance of species.

In the drainage basin of one small river in the center of the North American continent, one can find Kirtland’s warbler, which has a total population that seems to fluctuate around a few thousand individuals. In that same area, or indeed almost anywhere else east of the Rocky Mountains up until about 200 years ago, the passerine pigeon thrived with a total population size estimated in the low billions (1). This six-orders-of-magnitude discrepancy begs an explanation, especially once we notice that this seems to be one of ecology’s few universal laws (see the figure). Every ecosystem in the world, whether at the bottom of the sea or the middle of the Amazonian rain forest, has a few hyperabundant species and many relatively rare species (2). Understanding why a species has a particular abundance is the embarrassing and obvious question that ecology cannot yet answer.

On page 812 of this issue, Shipley et al. take a good first step toward an explanation (3). The setup is simple. Twelve vineyards were abandoned in southern France over a period ranging from 2 to 42 years ago. These yards slowly returned to natural vegetation, and the relative abundance (percentage of the total plant population \(p_{1} \ldots p_{30}\)) of 30 plant species in these plots was counted. The authors also measured a suite of eight characteristics or traits, such as perennial versus annual, thickness of leaf, and height of plant for each species (\(t_{\text{trait,species}}\)), for a total of 240 \(= 8 \times 30\) trait measures. They then calculated the average values of these eight traits (\(t_{\text{trait,avg}}\)) for each vineyard as a whole, using the equations:

\[
\begin{align*}
  t_{\text{height,avg}} & = \frac{1}{30} \sum_{i=1}^{30} p_{i} t_{\text{height},i} \\
  t_{\text{leaffhickness,avg}} & = \frac{1}{30} \sum_{i=1}^{30} p_{i} t_{\text{leaffhickness},i}
\end{align*}
\]

Next, Shipley et al. showed something elegant: These average traits show orderly change over time as the vineyards return to