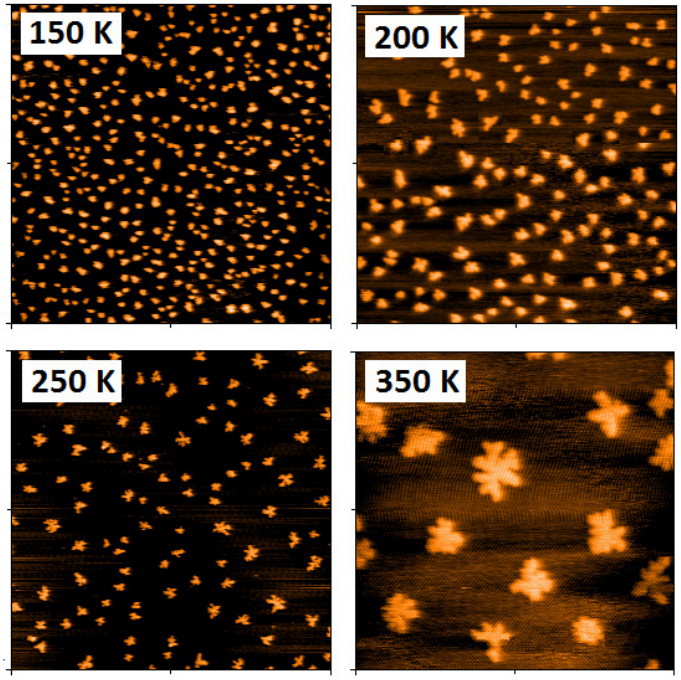
Theory Details How 'Hot' Monomers Affect Thin-film Formation

Like a baseball player sliding into third, a hot monomer skids in a straight line along a cold surface until it's safely among its fellow molecules.



Two-dimensional formations of pentacene on a mica substrate illustrate how "islands" form at different temperatures when grown via chemical vapor deposition. Experiments carried out at the Institute of Solid State Physics at Graz University of Technology, Austria, led a team of theoretical physicists at Rice University and the University of Maryland to form a mathematical model that describes how such islands form, depending on the temperature of the substrate and the rate of the island molecules' deposition. The images show areas 8 microns wide, with the exception of the 200 kelvin image, which is 4 microns wide. (Credit: Adolf Winkler/Graz University)

This is not what usually happens when scientists assemble monomers to make thin films for next-generation electronics, but the details remained a puzzle until a team of researchers from Rice University and the University of Maryland got involved. In this case, the monomers are organic molecules that form clusters and eventually complete layers.

The researchers devised the first detailed model to quantify what they believe was the last unknown characteristic of film formation, through physical vapor deposition on a mica surface cleaved with adhesive tape and then placed in an ultra-high vacuum chamber. Their work was published Dec. 10, 2014 in the journal *Physical Review Letters*.

"Our model shows that the growth of monomer islands and the evolution of nanostructures on surfaces can be far more subtle than commonly thought," said Theodore L. Einstein, a UMD physics professor.

Einstein co-authored the paper with UMD physics graduate student Josue Morales-Cifuentes, and Alberto Pimpinelli, executive director of the Rice Quantum Institute, a faculty fellow in the Rice Materials Science and NanoEngineering Department, and a visiting professor in the UMD Department of Physics.

Scientists make films as thin as a single molecule in the same way they make graphene: They heat a gas in a furnace and wait for its bits to condense and aggregate into a solid. Molecules in the gas hit a surface (typically mica in experiments, often silicon in applications) called a substrate, where they accumulate into a regular lattice.

Usually, organic molecules drawn by weak van der Waals forces alight on the substrate and skitter randomly from one point to another under the influence of vibrations in the substrate's crystalline lattice until they bump into another molecule or, more likely, an island of other molecules to join.

Islands that gather enough monomers create a critical nucleus: Take one away and the island could disintegrate; add one and the nucleus becomes a stable structure able to join with other growing islands to form the film.

Researchers understand how this happens, but when the substrate is cool enough to dampen its natural vibrations (for para-hexaphenyl—nicknamed 6P—on mica, at about minus 190 degrees Fahrenheit) and the gas is hot enough, the molecules hit the substrate and skid in a straight line along its surface, which scientists call ballistic motion. If they skid to a stop, they will wander until they find an island—or growing islands find them.

"The common wisdom has been that when molecules or atoms arrive at a substrate, their kinetic energy immediately dissipates into the substrate crystal," Pimpinelli said. "Their energy is essentially zero when they arrive at the surface, and they diffuse at random. But what happens if they don't, if the energy is preserved long enough that the molecule keeps its velocity at the surface and continues on in a line? Traditionally, this aspect has been totally neglected."

These skidding molecules can make islands grow, or knock other molecules off islands at or below the critical nucleation stage, perhaps even causing them to disassociate, Pimpinelli said.

Pimpinelli said nobody had successfully created a mathematical model that detailed the conditions under which ballistic, "nonthermal" motions could continue even after a molecule is adsorbed by the substrate.

"We already had a powerful mathematical framework for aggregation on surfaces," he said. "We have ways to describe in a lot of detail what happens to atoms, and can transfer those models lock, stock and barrel to these molecules—except for one: the 'hot' monomer.

The speed of island growth affects their size, which in turn affects the size of the electrically significant boundaries that form when they come together. These grain boundaries tend to decrease the electrical and thermal conductivity of a material.

"There is a simple 'scaling' relationship between the speed at which molecules are deposited on a surface and island density," said Einstein. "Everyone believed that this relationship increased smoothly between the low- and high-deposition regimes; however, our findings show that the relation in the intermediate regime is much more complex and one can easily be fooled."

The study originated when Pimpinelli's experimental associates in Austria observed that when they tried to grow films of rod-like 6P molecules on cold substrates, clusters would form in a way that was only compatible with ballistically moving monomers. 6P molecules are of special interest because of their applications to blue-light diodes and nano-optic devices, according to Einstein.

Quick calculations involving the temperature of the substrate and the deposition rate of the monomers suggested the system could be modeled; more complex mathematics not only confirmed it, but also provided a way to predict how various molecules and substrates will interact at specific temperatures.

"By studying how the number of islands changes with these control parameters, one is able to know the size of the critical nucleus, the diffusion process, all the energies involved and how these molecules bind to each other and the substrate," Pimpinelli said. "All the information, in principle, can be extracted by counting the islands on the surface."

In future work, Einstein plans to test the viability of the model with other experiments that show well-defined scaling in intermediate regimes.

"It would be interesting to extend the approach to non-standard surfaces having fractal dimension or quasicrystallinity," Einstein added.

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The research paper, "How 'Hot Precursors' Modify Island Nucleation: A Rate-Equation Model," Josue R. Morales-Cifuentes, T. L. Einstein and A. Pimpinelli, was published Dec. 10, 2014 in *Physical Review Letters*.

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