Science of building sandcastles finally understood

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A sandcastle on the beach which is held together by the universal process called capillary condensation. Credit: 'Hello I'm Nik' on Unsplash

Water vapor from ambient air will spontaneously condense inside porous materials or between touching surfaces. But with the liquid layer being only a few molecules thick, this phenomenon has lacked understanding, until now.

Researchers at the University of Manchester led by Nobel Laureate Andre Geim—who, with Kostya Novoselov, was awarded the Nobel Prize for Physics 10 years ago this month—have made artificial capillaries small enough for water vapor to condense inside them under normal, ambient conditions.

The Manchester study is titled "Capillary condensation under atomic-scale confinement," and will be published in *Nature*. The research provides a solution for the 150-year-old puzzle of why capillary condensation, a fundamentally microscopic phenomenon involving a few molecular layers of water, can be described reasonably well using macroscopic equations and macroscopic characteristics of bulk water. Is it a coincidence or a hidden law of nature?

Such properties as friction, adhesion, stiction, lubrication and corrosion are strongly affected by capillary condensation. This phenomenon is important in many technological processes used by microelectronics, pharmaceutical, food and other industries—and even sandcastles could not be constructed if not for capillary condensation.

Scientifically, the phenomenon is often described by the 150-year-old Kelvin equation that has proven to be remarkably accurate, even for capillaries as small as 10 nanometres, one-thousandth of human hair's width. Still, for condensation to occur under normal humidity of say 30% to 50%, capillaries should be much smaller, of about 1 nm in size. This is comparable with the diameter of water molecules (about 0.3 nm), so that only a couple of molecular layers of water can fit inside those pores responsible for common condensation effects.

The macroscopic Kelvin equation could not be justified for describing properties involving the molecular scale and, in fact, the equation has little sense at this scale. For example, it is impossible to define the curvature of a water meniscus, which enters the equation, if the meniscus is only a couple of molecules wide. Accordingly, the Kelvin equation has been used as a poor-man's approach, for the lack of a proper description. Scientific progress has been hindered by many experimental problems and, in particular, by surface roughness that makes it difficult to make and study capillaries with sizes at the required molecular scale.

To create such capillaries, the Manchester researchers painstakingly assembled atomically flat crystals of mica and graphite. They put two such crystals on top of each other with narrow strips of graphene, another atomically thin and flat crystal, being placed in between. The strips acted as spacers and could be of different thickness. This trilayer assembly allowed capillaries of various heights. Some of them were only one atom high, the smallest possible capillaries, and could accommodate just one layer of water molecules.

The Manchester experiments have shown that the Kelvin equation can describe capillary condensation even in the smallest capillaries, at least qualitatively. This is not only surprising, but contradicts general expectations as water changes its properties at this scale and its structure becomes distinctly discrete and layered.

"This came as a big surprise. I expected a complete breakdown of conventional physics," said Dr. Qian Yang, the lead author of the *Nature* report. "The old equation turned out to work well. A bit disappointing but also exciting to finally solve the century old mystery.

"So we can relax, all those numerous condensation effects and related properties are now backed by hard evidence rather than a hunch that 'it seems to work so therefore it should be OK to use the equation.'"

The Manchester researchers argue that the agreement, although qualitative, is also fortuitous. Pressures involved in capillary condensation under ambient humidity exceed 1,000 bars, more than that at the bottom of the deepest ocean. Such pressures cause capillaries to adjust their sizes by a fraction of angstrom, which is sufficient to accommodate only an integer number of molecular layers inside. These microscopic adjustments suppress commensurability effects, allowing the Kelvin equation to hold well.

"Good theory often works beyond its applicability limits," said Geim. "Lord Kelvin was a remarkable scientist, making many discoveries but even he would surely be surprised to find that his theory—originally considering millimeter-sized tubes—holds even at the one-atom scale. In fact, in his seminal paper Kelvin commented about exactly this impossibility. So our work has proved him both right and wrong, at the same time."

More information: Capillary condensation under atomic-scale confinement, *Nature* (2020). DOI: 10.1038/s41586-020-2978-1 , www.nature.com/articles/s41586-020-2978-1

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