

# Liquid marbles roll in tight places

Sometimes in southwestern France, a summer rain produces a slippery film of tiny balls called “summer ice” that roll around on the ground and resemble hail, but are instead made of liquid water. Now physicists Pascale Aussillous and David Quéré of the College of France in Paris have captured in the laboratory the phenomenon that creates summer ice. By coating water droplets with a thin layer of hydrophobic powder, they have produced liquid marbles that can travel swiftly across solids without wetting them. Such liquid marbles could expand applications of microfluidics in biomedicine and other fields.


It is difficult to push small amounts of water and other liquids through tubes or across surfaces, as microfluidics requires, because the liquids wet the surfaces and create high friction forces. In addition, as droplets move, they often leave some of the liquid behind, creating a cleaning problem because one liquid must be removed before another can pass through. To make the problem more manageable, researchers have tried to develop superhydrophobic coatings for solid surfaces so that water would not stick to them.

“I had been working on superhydrophobicity for three years when I decided that it would be more efficient to try to modify the surface of the liquid than that of the solid,” says Quéré. So he and Aussillous coated water droplets with a powder consisting of lycopodium pollen grains covered with fluorinated silanes. The powder clung to the droplets, but, being hydrophobic, was not wetted and did not allow the water through to wet the surface below, thus creating the

liquid marbles (*Nature* 2001, 411, 924).

Because the marbles do not wet the surface, they move like rubber balls—by rolling with little friction. The friction that they do encounter is created by the slight deformation that gravity creates in the spherical shape where it touches a surface. The smaller the droplet, the less the deformation; and under the influence of a given force, the droplets move faster and faster the smaller they are. “We used just slopes to move the particles about, but electrical or magnetic fields could easily be used as well,” Quéré points out.

When the droplets move fast enough, the centrifugal force acting on the liquid within them starts to deform their shape from a sphere into a peanut or dumbbell, and the droplets hop down an inclined surface. Sometimes a droplet assumes the shape of a torus or donut (but with a thin, rather than open, center) and rolls down the surface like a wheel. If the torus falls off the plane surface and falls freely through space, it resumes the peanut shape. Quéré is now trying to analyze quantitatively the conditions that create the various shapes.

Because the liquid marbles were so easy to form, and since pollen and water are abundant, Quéré guessed that the marbles exist in nature and later found them in the reports of summer ice. “These marbles should form as well when water falls on clay, so they might be an important phenomenon in soil erosion,” he speculates. Thus, an understanding of their behavior may not only help microfluidics but could aid in water management and soil conservation. 



A 1-mm-diam water droplet coated with a thin layer of hydrophobic powder rests temporarily on and deforms a water surface with its weight, like a liquid marble.

## Chaos in weather forecasts

It has long been known that the atmosphere is a chaotic system, one in which tiny changes in conditions at a given time can lead to exponentially growing changes. This has been termed the butterfly effect, after the not-too-exaggerated notion that the flapping of a butterfly’s wings can affect storm patterns several weeks later.

But even chaotic systems have degrees of predictability, and improving that predictability is essential in weather forecasting. A team of researchers at the University of Maryland in College Park, which includes meteorologists, physicists, mathematicians, and computer scientists, has found that applying chaos theory to the atmosphere may enhance forecast reliability (*Phys. Rev. Lett.* 2001, 86, 5878).

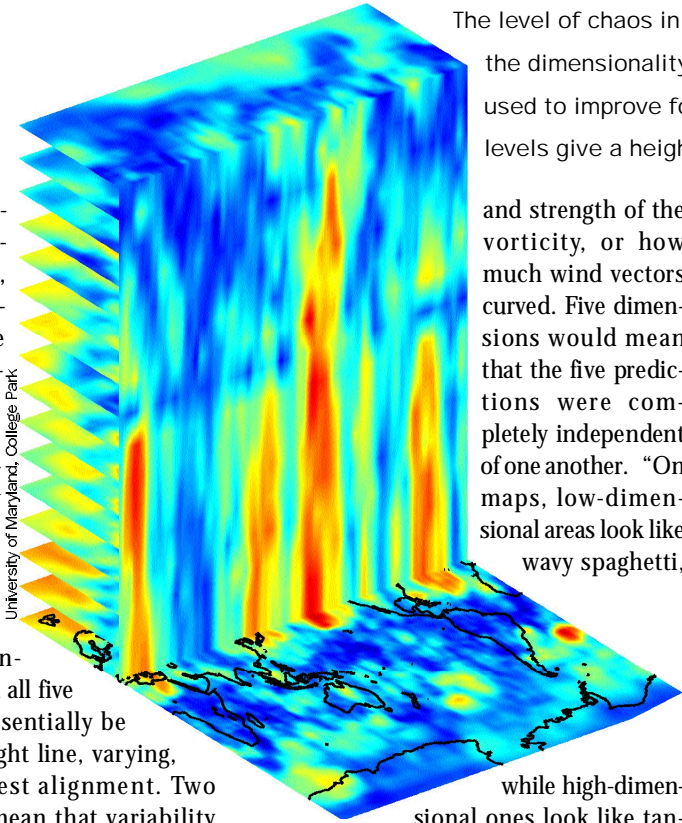
Their approach is based on the idea, common in chaos theory, that chaotic systems do not vary randomly through all possible states but vary in a select number of ways, which can be expressed in terms of a limited number of mathematical dimensions. The National Weather Service (NWS) has a ready-made database to study how this chaotic dimensionality changes with time and place. The NWS feeds a vast amount of observed weather data into a complex computer simulation of the world’s atmosphere. The model then produces predictions of winds, atmospheric pressures, precipitation, and temperatures for one to sixteen days in the future. At regular time intervals, the NWS modifies the input data by small amounts to produce five “perturbed” forecasts, to see how much they differ from the original forecast, or main solution. In regions where the perturbed solutions vary a great deal from the main solution, the reliability of the original prediction is the lowest (see map).

“What we did was to represent each 1,100 km<sup>2</sup> in each perturbed prediction of wind patterns at a given level by a vector. This vector consisted of the east–west and north–south wind components at 25 points within the square,” explains D. J. Patil, one of the researchers. The team’s program then

The level of chaos in a forecast can be characterized by the dimensionality. Low dimensionality (red) can be used to improve forecasts. Calculations at multiple levels give a height perspective.

compared the five perturbed or “bred vectors” for a given square, using a standard statistical technique called principal component analysis.

For each grid point, this procedure measured how many dimensions, from one to five, could best describe the variability among the five predictions. One dimension would mean that all five predictions could essentially be arrayed along a straight line, varying, say, only in east–west alignment. Two dimensions would mean that variability could be described by two independent measures, such as east–west alignment



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and strength of the vorticity, or how much wind vectors curved. Five dimensions would mean that the five predictions were completely independent of one another. “On maps, low-dimensional areas look like wavy spaghetti,


while high-dimensional ones look like tangled spaghetti,” says Patil. The team found that there were areas of

low dimensionality, with around two dimensions, that concentrated in several regions, such as North America. These areas often moved west to east with the weather patterns themselves. Overall, dimensionality seemed much lower in the Northern Hemisphere than in the Southern, although Patil is still unsure whether this is a real effect or just a consequence of the way the data are gathered.

“By isolating an area of low dimensionality, and showing what those dimensions are at a given point, we can help the NWS to order specific measurements that can be used to distinguish among the possible predictions,” explains Patil. “The goal is to pinpoint where the uncertainty lies and what measurements are needed to decrease it.”

In regions of high dimensionality, such measurements cannot be easily specified, but at least weather forecasters would know that forecasting reliability for these regions

would be low. “We could help the forecaster decide how far in advance a forecast might be valid when the weather dimensionality was high—for example, when five-day forecasts would be unreliable,” says Patil. At present, the NWS estimates the reliability of forecasts, but current policy is not to publicize such estimates.

Currently, Patil and colleagues are studying a larger number of perturbations, up to 100 at a time. If they still find regions of low dimensionality, they may be well on the way to developing a tool that can take some of the chaos out of weather forecasting. 

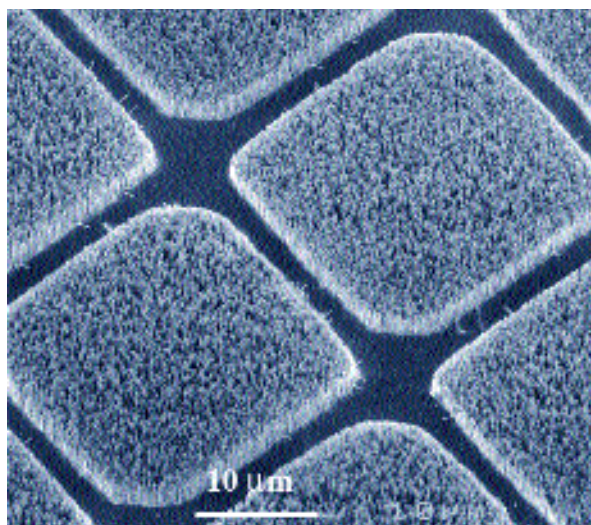
## Ultraviolet nanolasers

**W**ith blue diode lasers moving rapidly toward mass production, researchers have naturally turned to the development of ultraviolet (uv) diode lasers. Such lasers would have the same advantages as did previous moves to shorter wavelengths: the shorter the wavelength, the more data one can pack in a given area of an optical disk. But it has not been obvious what material would be suitable for such lasers. Now researchers from Lawrence Berkeley National Laboratory and the University of Califor-


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When a gold coat on a sapphire substrate is heated, zinc oxide crystals can be grown vertically to form a forest of nanowires with a density of  $10^{10}/\text{cm}^2$ , suitable for ultraviolet diode lasers.

trying to dope impurities into the ZnO to form a p-n junction, a standard part of a Nd:YAG laser diode. 

## Photonic transistor

In optical communications, optically carried data frequently must be converted to electricity, amplified, and then converted back to optical signals. This double conversion


slows transmission and adds expense and complexity. For both optical communications and optical-computing concepts, it would be better to manipulate data while keeping it in optical form. Doing so, however, requires an optical transistor, one that allows the light from one laser to directly control the light from another, with no electronic steps in between.

At the National Institute of Advanced Industrial Science and Technology (Tsukuba, Japan), Junji Tominaga and colleagues, collaborating with researchers at the Sharp Corp. (Nara, Japan) and TDK Corp. (Nagano, Japan), have taken a step in developing such a photonic transistor, based on a new kind of optical disk. Although the device does use electric fields

as an intermediary between the two laser beams, it does not use the traditional route of amplification of electric currents. Rather, it generates direct modulation of a reflected light beam.

The device uses surface plasmons, which are electrical field waves generated by the motion of electrons in a metal or semiconductor. A plasmon is generated on a specially designed optical disk when it is irradiated with blue laser light. The interaction of the plasmon with the light beam in a layer of silver oxide creates small silver scattering centers. When red laser light is used to read the disk, the presence of the scattering centers increases the reflected signal by up to 60-fold. Thus, the presence or absence of the blue laser light modulates the output of the reflected red laser beam, just as a gate signal in a transistor modifies the output signal. The process is fully reversible: when the blue laser light is shut off, the silver particles recombine with oxygen to form silver oxide, eliminating the scattering centers (Appl. Phys. Lett. 2001, 78, 2417).

“We can produce the scattering centers with a low laser power of only 3 to 4 mW,” Tominaga reports. “But for a practical device, we need fast switching speeds.” Tominaga estimates that switching speeds of the device currently may be around 35 MHz, well below the multi-hertz speeds needed for communications.

Although the present version of the device is not likely to be directly applicable to communications, it could point the way to faster devices in the future. 

When red laser light is used to read this optical disk, scattering centers created by the interaction of a plasmon with blue laser light increase the reflected signal by up to 60-fold.

nia, Berkeley, have demonstrated uv lasing in zinc oxide (ZnO) nanowire arrays, in which each nanowire is only 20 to 150 nm in diameter.

Zinc oxide has the wide bandgap (3.37 eV) needed to emit uv photons. Equally important, it can lase through the recombination of electron-hole pairs (excitons), a more efficient process than that in most existing laser diodes. By producing lasers in the form of nanowires with dimensions smaller than the 385-nm wavelength emitted, the team has created a natural resonator cavity that makes it easier for the crystals to lase (Science 2001, 292, 1899).

To create highly regular arrays of the nanocrystals, the researchers first coat a sapphire substrate with a layer of gold. When the gold is heated, it melts and aggregates into billions of droplets, each only tens of nanometers across. At a temperature near 900 °C, a powdered mixture of ZnO and graphite reacts to produce zinc vapor, which dissolves in the gold droplets and deposits ZnO crystals on the sapphire.

Because the crystalline spacing of ZnO and sapphire almost exactly match along one direction, the ZnO crystals grow up precisely vertically to form a forest of nanowires with a density of  $10^{10}/\text{cm}^2$ .

Using this array, the researchers demonstrated lasing action when the crystals were optically pumped with a frequency-quadrupled Nd:YAG laser.

Of course, for practical operation, uv diode lasers will have to be electrically pumped, and the team is now

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