Mysterious Nanoscale Forces

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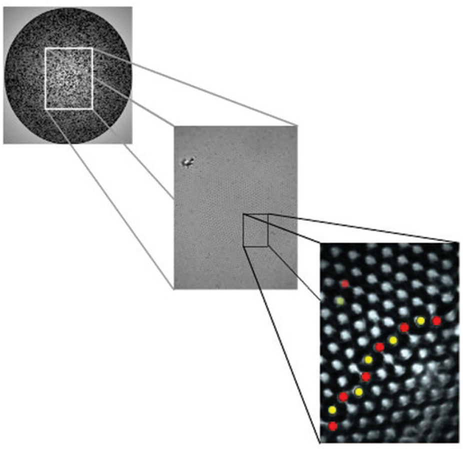
Every child knows that 1+1 equals more than zero, so researchers from the University of Stuttgart were shocked by the results of an experiment in which putting together two repulsing forces created an attraction instead of the expected stronger repulsion. Can enhancing repulsion forces really result in attraction?

In an ingenious experiment, the Stuttgart researchers measured the interactions between charged colloidal particles and a surface with the same electrical charge. Next, the fluid the particles were immersed in was brought to a specific state in which it induced the thermodynamic Casimir effect. Previous studies have shown that this force repels electrically neutral plates, with one plate showing a greater attraction for water and the other for organic substances. However, in this case, unipolar charges on the hydrophilic particle and on the hydrophobic surface resulted in an attraction rather than the expected repulsion.

The results of the experiment were so unexpected that the present author and Faezeh Pousaneh, a doctoral student taking part in the International Doctoral Projects of the Foundation for Polish Science, decided to check them against predictions made by statistical mechanics, describing systems with high numbers of particles. Working with Dr. Anna Maciołek from Stuttgart, they made appropriate assumptions and approximations allowing them to introduce equations which could be solved analytically. Their solutions confirmed that attraction should indeed occur at a certain narrow temperature range. The results of the theoretical calculations also allowed them to discover why this happens, and explain this odd phenomenon without using any formulae.

Hydrophilia and hydrophobia

Colloidal particles are a fraction of a micrometer long; in comparison with water molecules, they are like beachballs vs. grains of sand. They occur naturally, for example in milk. In a colloidal crystal, particles arrange themselves such that their repulsion is balanced with attraction, as is the case for atoms in ordinary crystals. If it were possible to guide the forces acting on the particles, it would also be possible to stimulate spontaneous formation of colloidal crystals with the desired structure and properties which could be adjusted according to requirements. Ordinary forces are too weak, but interactions between the particles can be mediated by the fluid in which they are immersed, as long as phase changes are used. Water and alcohol are miscible at all proportions, while water and oil are not. For some organic substances, the boundary of their miscibility with water, known as their critical temperature, is the same as room temperature. At the critical temperature, water and the organic substance no longer form a uniform fluid, and start dividing



Mark Bowick and Angelo Cacciuto (Syracuse University), NSF

Diagram of a water droplet covered with a colloidal crystal

Enhancing repulsion to obtain attraction?

IChF PAN, Grzegorz Krzyżewski

Faezeh Pousaneh, doctoral student from the PAS Institute of Physical Chemistry in Warsaw, with a culinary version of the mixture she studied. The fruit symbolize colloid particles, white grains – water, dark grains – lutidine, and red grains – hydrophilic ions

into two fluids of different compositions. When two plates are immersed in a fluid close to the critical point, with one of the plates being hydrophilic and the other hydrophobic, the former will be covered with a neutralizing film of water, the other with the organic substance. The closer to the critical temperature, the thicker the films. They behave similarly to the individual particles: the water film "likes" water and "hates" oil. This is why two hydrophilic plates are attracted to one another, while a hydrophobic and hydrophilic one repulse. The range of these forces is similar to the thickness of the adsorbed layers, and increases with the approaching critical temperature.

Key salts

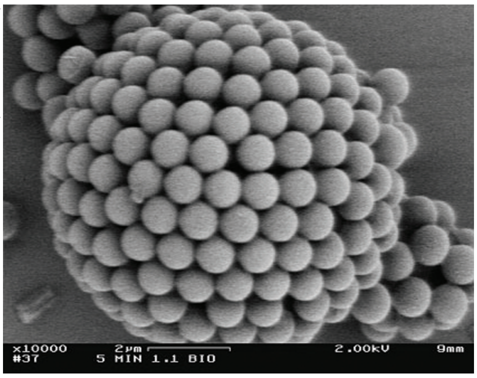
For two hydrophilic particles, the attractive Casimir effect, superimposed onto electrostatic repulsion, is similar to the forces between atoms, albeit on a greater scale. In the experiment conducted at Stuttgart, salt was added to the solution in order to reduce the range of electrostatic repulsion. The salt ions surround the particle and neutralize its charge. Due to thermal movement, the layer containing the neutralizing charge is thick; however, it can be reduced by increasing the number of ions in the solution. At a distance greater than the thickness of the neutralizing film, the electrostatic force practically disappears, but this does not occur at lower distances, since it is not fully shielded. Following the addition of salt, the equilibrium distance between hydrophilic particles was reduced. It was also noted that the hydrophobic particle was attracted to a water-coated surface with the same charge.

While constructing a mathematical model, the researchers took into consideration that salt is soluble in water only. This fact turned out to be key in explaining the mystery. While calculating the concentration of the solution at various distances from the charged surface repealing water, they noted a surplus of the organic substance in its vicinity, and a surplus of water a little further away. The second hydrophilic surface encountering this water surplus started attracting it, and with it the second surface, as though it was also hydrophilic. Importantly, attraction was also the result of the calculations. In turn, repulsion appeared again as the temperature approached critical. However, in this case there was no surplus of water near the hydrophobic plate.

Fight for territory

Where does the water near the hydrophobic plate originate from? The hydrophobic plate powerfully attracts the organic substance, but the charge on the plate has a powerful attraction to ions. However, the ions cannot penetrate the organic substance. There is competition for access to the plate among components that cannot occur next to one another, not unlike hostile tribes fighting for prime riverside territory. A compromise is achieved by the plate attracting ions, together with the water molecules that surround them. The whole "packet" of ions and water arranges itself just beyond the organic layer. Nearer the critical temperature, the organic layer becomes too thick, and electrostatic forces are not sufficient to generate a surplus of water. Following the earlier analogy, it is as though the most powerful tribe had set up a city by the river, while the other two build a settlement in the suburbs, attracting fellow tribesmen from other parts. The city then grows to absorb the settlement, whose former inhabitants cease to be in the majority. Now the settlement only attracts the dominant tribe.

David Weitz research laboratory at Harvard University



Colloidosome viewed through an electron microscope: a water droplet covered with colloid particles

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Colloid particles occur in nature, for example in milk

1 + 1 > 0

Of course 1 plus 1 equals more than zero, and it is complex physical phenomena that are responsible for the fact that the left side of the equation appears to be quite different in this experiment. Explaining these apparent paradoxes from first principles is highly satisfactory, in particular given that a greater understanding of the phenomena can lead to the discovery of practical applications for them. The discovery of a water-repelling surface which exhibits hydrophilic properties at certain temperatures may well prove useful. ■

Further reading:

Pousaneh F., Ciach A. (2011). The origin of the attraction between like charged hydrophobic and hydrophilic walls confining a near-critical binary aqueous mixture with ions. J. *Phys.: Condens. Matter*, 23, 412101-1-412101-5.

Hertlein C., Helden L., Gambassi A., Dietrich S., Bechinger C. (2008). Direct measurement of critical Casimir forces. *Nature, 451*, 172-175.

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