Manipulation of atoms, molecules, and fluids at the nanoscale.

- arXiv:1606.09051
  Molecular transport through capillaries made with atomic-scale precision, B. Radha, A. Esfandiar, F. C. Wang, A. P. Rooney, K. Gopinadhan, A. Keerthi, A. Mishchenko, A. Janardanan, P. Blake, L. Fumagalli, M. Lozada-Hidalgo, S. Garaj, S. J. Haigh, I. V. Grigorieva, H. A. Wu, A. K. Geim, Nature, doi:10.1038/nature19363 (2016).

- arXiv:1511.06693
  Sieving hydrogen isotopes through two dimensional crystals, M. Lozada-Hidalgo, S. Hu, O. Marshall, A. Mishchenko, A. N. Grigorenko, R. A. W. Dryfe, B. Radha, I. V. Grigorieva, A. K. Geim, Science **351**, 68 (2016).

Recommended with a commentary by F. Guinea, Imdea Nanscience, Madrid.

The above articles, and others mentioned below, describe the extensive work done at the University of Manchester on the design and characterization of novel devices for the manipulation of atoms and fluids at the nanoscale. They make use of the unique properties of two dimensional materials, especially graphene. The results reported in these papers pose a number of interesting problems in fundamental science, as they probe regimes not previously studied.

The extreme stiffness and stability of graphene and other two dimensional materials allows for the design of devices where critical dimensions can be less than 1 nm, and with a high precision. These devices range from sieves, to ultra thin two dimensional containers, and nanoscopic capillaries. The materials which are trapped within these devices, or that flow through them, present unusual features, some of which are not yet fully understood.

The article by Radha *et al.*, reports the fabrication of capillaries with atomic scale precision. These capillaries are patterned using photolithographic methods. They also measure molecular and ionic transport through capillaries of different thicknesses. Substances with large molecular or ionic radii are blocked in narrow capillaries, and flow freely in wider ones. These devices open up the possibility of filtering and detecting minuscule amounts of compounds in solution. Moreover, the flow rate is rather large in narrow capillaries, suggesting that boundary effects play a significant role.

The results of Radha *et al.* confirm and extend considerably the findings reported in[1,2], where filters made up by graphene oxide membranes were studied. These filters, of an area of order of 1 cm^2 and a thickness of a few microns, were used to separate fluids with ions in suspension. Graphene oxide membranes, in the absence of water, are impermeable. Reference[1] showed that the graphene oxide filter allowed the passage of ions of small radii (the so called hydrated radius takes into account the screening cloud which surrounds the ion), but prevented very efficiently the passage of dissolved ions and molecules with large

radii. The likely explanation was the existence of extremely narrrow capillaries, a few nanometers thick, which impede the flow of the large ions, as confirmed by Radha *et al.*

The paper by Lozada-Hidalgo *et al*, measured the transmission rates for protons and deuterons through membranes of atomic thicknesses. As in the previous experiment, graphene and BN were used. The rates for the two isotopes differ by about one order of magnitude, irrespective of the membrane. This result suggests that quantum effects play a role, as thermal activation should give the same rate for the two isotopes. It is worth noting that this quantum effect is observed at room temperature. Reference[3] previously studied proton transport through different atomically thin membranes. Monolayer graphene and BN are excellent proton conductors, while thicker multilayers and other 2D materials, such as MoS_2, are not. Moreover, the transport rate for graphene exceeds significantly the rate obtained from calculations of the barrier height and shape, suggesting a non trival transmission path.

The structure of water tightly confined between flat graphene layers was studied in[4]. These layers are a few nanometers apart, and exert a very high pressure on the water molecules. A simple estimate in the paper gives $P \sim E_{VdW}/d$, where E_{VdW} is the Van der Waals energy per unit area between graphene layers, and d is the distance between them. Ths estimate gives $P \gtrsim 1$ GPa, $\approx 10^4$ atm. This pressure is enough to turn the water into " square ice " even at room temperature. It is worth noting that theoretical two dimensional square ice is a model widely studied for the understanding of the residual entropy of ice at low temperatures. It was proposed in ref.[5] and solved exactly in ref.[6].

The study the Van der Waals pressure exerted in materials trapped between atomically thin layers was further studied in refs.[7] and [8]. Ref.[7] measures the pressure on encapsulated molecules by using the sensitivity of Raman active modes to the applied pressure. They find pressures $P \approx 1.2$ GPa. This reference also found that such pressures can induce chemical reactions, and modify the confined substances, so that confinement leads to nanoscale "chemical reactors". Finally, ref.[8] studied the shape and pressure in bubbles which are inevitably formed when an atom thin layer is deposited on a substrate. Typically, residual hydrocarbons from the fabrication process are trapped inside these bubbles. The shape of the bubbles is determined by the balance between elastic forces, which tend to make them flat, and the cost in Van der Waals energy, which tends to reduce their base. The fact that the two dimensional elastic constants and the Van der Waals energy have the same dimensions (Energy Area^{-2}) leads to the existence of a universal shape for the bubbles, irrespective of size and pressure. The pressure, on the other hand, depends on the volume, as $P \sim V^{-1/3}$, and it can reach values of hundreds of MPa.

In summary, the observations reported above present many interesting fundamental challenges, such as the influence of boundary conditions on fluid flow at the nanoscale, the role that elastic and adhesion forces play in these devices, the phase diagram of two dimensional matter at high pressure, quantum effects at room temperature, ...

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