MOLECULAR MACHINES

Knowledge is power!

A molecular motor inspired by Maxwell's demon can be driven away from equilibrium using the information provided by the location of one of its interlocked components.

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The molecular ratchet is a seductive concept for nanoscientists. If particles can be made to travel past a barrier in just one direction, pressure will build at the receiving end, which can, in principle, be used to perform useful work. A spring-loaded one-way gate that fast-moving molecules can push open and pass through would be especially attractive. The energy needed to create the pressure differential could simply be drawn from random thermal motion. Sadly, such a system — an archetypal perpetual motion machine — is impossible. Experiment[1] and theory[2,3] both show that molecular ratchets move with equal ease in either direction, however asymmetric they may seem. This is hardly surprising since the overall process (conversion of ambient thermal energy to work) contravenes the Second Law of Thermodynamics[4].

Suppose, however, that the gate can be opened deliberately and selectively for molecules approaching from one side. In James Clerk Maxwell's classic thought experiment, a miniature demon acts as a gatekeeper between two compartments containing molecules in random motion. The demon can perceive molecules heading for the gate, and can open it to let them through. He chooses to do this only for molecules in one of the compartments. As a result, molecules accumulate in the other compartment, creating unequal pressures and shifting the system from equilibrium.

Although Maxwell originally thought otherwise, it turns out that the demon does not break the Second Law, because in performing his task he must dissipate energy[5]. Maxwell's demon is thus a theoretically viable agent for transforming energy into work on the molecular scale. The problem, of course, is that demons of the right type are hard to find. Now, writing in *Nature*, David Leigh and co-workers from the University of Edinburgh show that a molecular system with some similarity to Maxwell's can be put into practice[6].

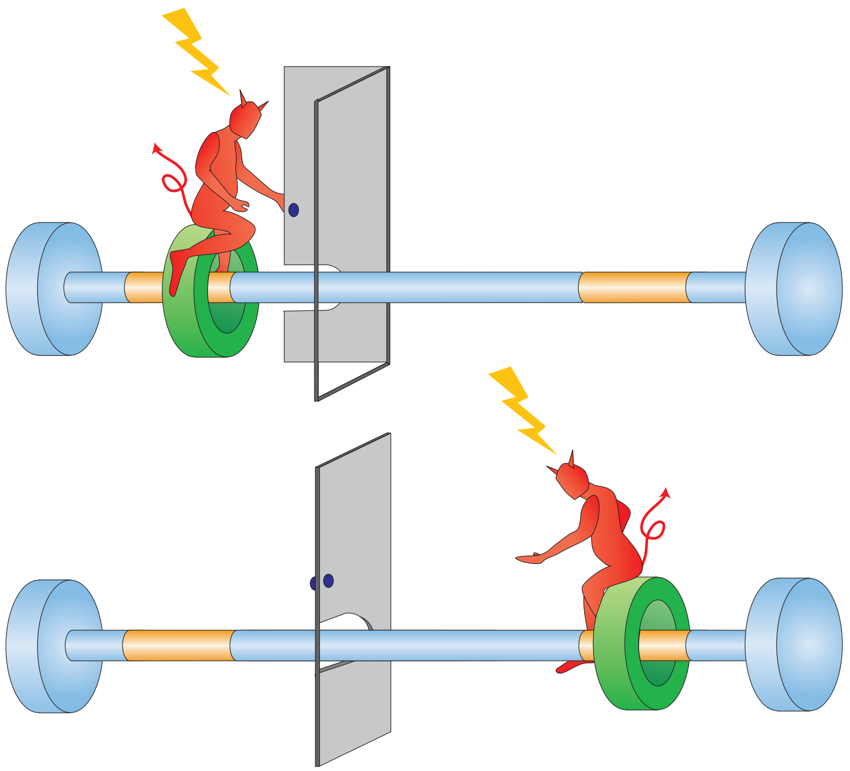

Figure 1 A schematic representation of the 'information ratchet' of Leigh and co-workers. The ring (green) can move along the axle (blue) provided that the gate (door) is open. The ring carries a mechanism for opening the gate (the demon) that is activated when energized by light, but this only works when the demon is close to the gate. The axle incorporates binding sites (orange) for the ring, and the site on the left is much closer to the gate. From the left-hand station the demon can open the gate, but from the right-hand station he cannot reach. The ring thus spends more time on the right, even though thermodynamics dictates that it should spend more time on the left.

Popular with researchers who make synthetic molecular machines are rotaxanes — assemblies consisting of 'rings' threaded onto 'axles' and kept in place by large blocking groups. In Leigh's case, his rotaxane is an organic molecule, with a single ring trapped on an axle (Fig. 1). The axle possesses three additional features, a 'gate' (depicted as a door in Fig. 1) — which, when closed, prevents the ring from passing from one side of the axle to the other — and two binding sites around which the ring preferentially sits. The affinity of the ring for the left-hand binding site is slightly greater than for the one on the right and so in a large ensemble of these molecules at thermodynamic equilibrium, 65% of them will have rings sitting on the left and 35% will have them on the right. The special feature of this system is that when it is exposed to ultraviolet light, the distribution of the rings changes — a greater proportion of them become trapped on the right-hand side of the molecule and the system is pushed away from its equilibrium position. The key to this is the operation of the gate.

In molecular terms, the gate is an alkene (a carbon–carbon double bond) that can be isomerized between two different geometries — the '*cis*' form puts a kink in the axle and represents a closed gate, whereas the straighter '*trans*' form corresponds to the gate being open and allows passage of the ring. Leigh and co-workers have designed their system so the ring contains a photosensitizer that converts light into the energy necessary to 'open' the gate. The directional asymmetry (ratcheting) arises because the gate is placed much closer to one binding site than the other, and the process that opens the gate depends upon the distance between it and the ring. The ring is able to pass along the axle fairly freely, but it is attracted to the binding sites and spends most of its time in these two locations. When sitting on the left-hand binding site, the ring is near the door and can easily open it. When the ring sits on the right-hand binding site, however, it is further away from the gate and so opening it becomes much more difficult.

As shown in Fig. 1, one might envisage the photosensitizer to be a demon riding on the ring, reaching out to open the door. Located on the left-hand binding site he succeeds, but on the right-hand side the distance is too great. Therefore, when the ring is on the left, the door is open quite often, allowing thermal motion to carry the ring through to the right. When the ring is on the right, however, the door is mostly closed, so the ring is less likely to pass to the left. The net result is that the ring spends more time on the right. In analogy with Maxwell's pressure demon, the imp that does Leigh's bidding only opens the door for molecules passing from left-to-right and not right-to-left. The rings do not all end up on the right-hand side, however, because there are other non-demonic mechanisms by which the door can be opened allowing movement back to the left.

This system is distinctive in that, although energy is necessary, it is not applied directly to the moving object. In most molecular motors, photonic[7,8] or chemical[9,10] energy is used to change a system's potential energy so that it moves into a new state (changes shape). Effectively, the moving part is pushed from one place to another. In a rotaxane this is usually reflected by a ring being shifted from one binding site to another. This can be achieved by changing the relative affinities of the two, and the system relaxing into a new equilibrium position. With Leigh's device, however, the ring's motion is Brownian — the result of random thermal energy. The energy supplied by the light is used, rather, to manipulate the barrier (gate) that controls the passage of the ring from one side to the other in a selective fashion, which drives the system away from equilibrium. The operation of the gate is 'information-dependent', as opening it relies on 'knowledge' of the position of the ring. For this reason the system can be described as a 'molecular information ratchet'.

To realize their ideas, Leigh and co-workers had to solve a number of problems, not least the fact that their proposed photosensitive gate was open in its resting state, closing only in the presence of light and a photosensitizer. Their solution was to add a separate photosensitizer, of a different type, to the solution containing the rotaxane molecules. This second photosensitizer was especially effective at closing the gate, whereas the one attached to the ring was more inclined to open it. With the right choice of concentrations, the separate photosensitizer was able to dominate when the ring was stationed on the right hand binding site, whereas the internal sensitizer dominated when the ring was on the left. Thus, the gate was indeed open more often when the ring was on the left.

Owing to these complications, the effect — which was observed using nuclear magnetic resonance spectroscopy — was not especially large. The population of rings on the left decreased by approximately 30% when the light was shone on the rotaxanes, shifting the system away from the equilibrium distribution of roughly 65:35. Nevertheless, the principle of information-based ratcheting is clearly demonstrated. Applications may be some way off but these elegant experiments provide a first indication that Maxwell's demon can be harnessed by nanotechnologists.

References

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PHOTONIC DEVICES

Coaxing light into small spaces

Coaxial cables transmit radiation with a wavelength much bigger than their diameter. Now, a miniature version borrows this concept to carry visible light at the nanoscale.

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Researchers in nanophotonics are always greedy for more photons. This is certainly the case with near-field scanning optical microscopy (NSOM), a technique that offers spatial resolution several times smaller than the wavelength of light (400–700 nm in the visible range). In NSOM, a tiny aperture in an opaque film is used to illuminate and/or collect light from a surface. By scanning the aperture over the surface, it is possible to image the fluorescence from the surface or the transmission of light through it, with a resolution that is essentially limited by the width of the aperture.

NSOM provides researchers with information that is not accessible with conventional optical microscopy. Unfortunately, when the diameter of the aperture is less than about 10% of the wavelength, a rather heroic effort is required to collate a useful image. This is because the aperture in an opaque thick metallic film is effectively a hollow cylinder, or, in the language of optics, a waveguide. However, above a cutoff wavelength — about twice the diameter of the waveguide — the transmission decreases exponentially with the length of the cylinder.

The very low power throughputs of most commercially available optical probes pose a severe limitation to near-field techniques. But some light at the end of the tunnel — or