ability of living organisms, which maintains control of local environments through precise control and regulation of interconversions of chemical and mechanical energies[8,9].

As a consequence of the microscale nature of responsive hydrogel features, the system response is rapid and precisely controlled. With current advances in methodologies of polymer patterning[10], the design of the system could be readily combined with other microscale devices and adapted to a broad range of reactions and hydrogel compositions. The question to be addressed is to what extent the reported system can be integrated with

complex, hybrid, multiscale systems that may require a particular application of C1→M→C2 events, for example, the spatio-temporal release of reagents in multistep microfluidic reactions. In short, however, this new paradigm reported by Aizenberg and colleagues will significantly impact the field and pave the way for fundamental studies and exploration of applications of autonomous systems with C1→M→C2 coupling. ❑

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**MATERIAL WITNESS**

# TWO WAYS TO RELAX

"God made solids, but surfaces are the work of the devil", Wolfgang Pauli famously proclaimed. But he might equally have found a diabolical imprint in that slippery phase masquerading as a solid: the glass. Surfaces are complicated, but our understanding of them is rather profound in comparison with the glassy phase, which still lacks any comprehensive thermodynamic description. It's not even agreed whether a glass is best described in kinetic or thermodynamic terms, although Woodcock has claimed to have identified a unique, reversible path from a gas to a random close-packing, suggesting that this glass at least can be thermodynamically defined (L. V. Woodcock, *J. Phys. Chem. B* **116,** 3734–3744; 2012).

In general, though, the glassy phase has been considered contingent: a kinetically arrested arrangement of particles in a supercooled liquid, frozen in a rough and enormously degenerate energy landscape. In the simplest picture the dynamics of the glass are Arrhenius-like: the system relaxes, following a perturbation, via jumps between energy minima separated by a Gaussian distribution of free-energy barriers. In this case the relaxation time is proportional to the inverse of temperature.

But this isn't always what is observed. Some glassy systems can exhibit a switch, as temperature is

lowered, from Arrhenius dynamics to a different form, typically to 'super-Arrhenius' behaviour in which the relaxation time has a faster temperature dependence. This crossover has been described as a transition from a so-called strong to a fragile state (C. A. Angell, *Science* **267,** 1924–1935; 1995). Silica exemplifies a strong glass-former, whereas some polymers form fragile glasses. But the classification is phenomenological, with no clear indication of what it implies physically.

Hentschel and colleagues now offer such a picture (*Phys. Rev. E* **85,** 061501; 2012). They say that the two regimes are characterized by single-particle dynamics (Arrhenius) and collective, cooperative relaxation (super-Arrhenius).

The researchers follow the crossover using a simple model of a binary glass in which two types of particle interact via Lennard-Jones potentials. The vital new ingredient is that they use an approach for ensemble averaging that retains information about the statistics of the free-energy barriers. Rather than ensemble averaging the relaxation times (related to the exponential of the barrier height) from many simulations, they reduce the relaxation time for each run — which will differ from run to run — to the free-energy barrier before averaging, thus capturing the distribution of barrier heights.

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This reveals the replacement of one Gaussian distribution by another as the crossover is approached. Moreover, looking at the dependence of the crossover temperature on the system size allows a physical interpretation to be placed on the transition. At higher temperatures, relaxation involves a particle escaping from the 'cage' formed by its neighbours, with a certain activation energy. But at increasingly low temperatures there is also a second-neighbour cage, and perhaps a third shell too, so it becomes ever harder for the particle to relax. In effect, there's no longer an escape route.

What is then needed instead for escape is a cooperative rearrangement of many particles. To put it another way, the particles must together 'collect' enough free volume to enable the relaxation. This is perhaps still an excessively simplified picture, but nonetheless one that captures the main observed features of the strong-to-fragile transition. ❑