

## COLLOIDAL GELS

## Clay goes patchy

Empty liquids and equilibrium gels have so far been only theoretical possibilities, predicted for colloids with patchy interactions. But evidence of both has now been found in Laponite, a widely studied clay.

Willem K. Kegels and Henk N. W. Lekkerkerker

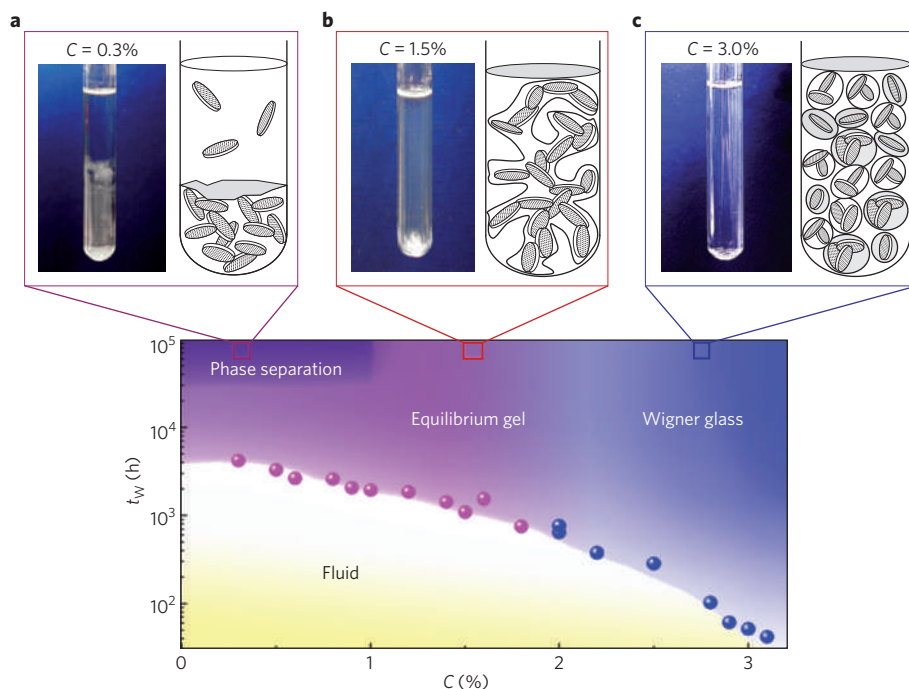
When designing computational models of the interaction between colloidal particles, isotropic potentials are the first and usual choice. In addition to simplicity, isotropy in interactions reflects the homogeneous surface properties of most colloidal particles synthesized in the laboratory. But significant progress has recently been made in modelling the behaviour of ‘patchy colloids’, as colloidal particles with their surfaces decorated with geometrically well-defined sticky spots are called. Yet so far patchy colloids exist mostly *in silico*<sup>1,2</sup> — that is, although there have been a few successful attempts in the laboratory<sup>3–5</sup>, an experimental counterpart is thought not to exist in nature. Or at least that is what everyone believed. Writing in *Nature Materials*, Ruzicka *et al.*<sup>6</sup> demonstrate that an experimental realization of patchy particles has been known for a long time but has only now been recognized: Laponite.

Laponite is an industrial synthetic (hectorite) clay that has been extensively studied as a model system<sup>7</sup>. Ruzicka *et al.*<sup>6</sup>, after years-long experiments, report that the topology of the phase diagram of Laponite in water, as well as the slow ageing behaviour of the system, is consistent with the behaviour predicted for platelets that interact with directional and anisotropic forces — that is, patchy interactions. After several months, at relatively low concentrations (less than 1% by weight) the initially fluid-like Laponite suspension spontaneously turns into a gel. But that is not the ultimate fate of the system: very slowly — on the timescale of years — it phase-separates into clay-poor and clay-rich states, the latter not being particularly concentrated (about 1% by weight). Indeed, increasing the Laponite concentration at constant volume leads to a first-order phase transition (Fig. 1): the clay-rich phase linearly grows with the overall Laponite concentration, eventually occupying the whole volume of the container. Such a homogeneous phase is an extremely stable gel — termed an ‘equilibrium gel’ by the authors<sup>6</sup> — as indicated by samples analysed over a period of seven years.

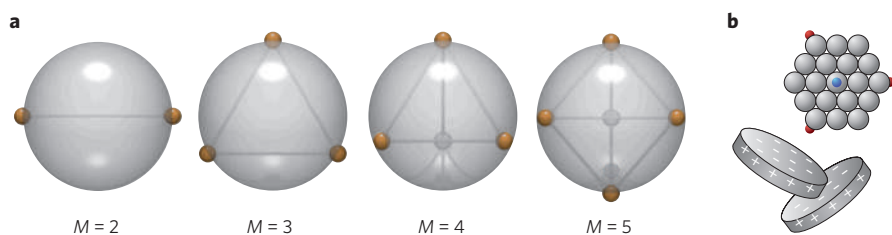
The dynamics of the formation of the equilibrium gel is completely different from that of the arrested phase separation observed in systems with gas–liquid instability, such as colloids with short-range, isotropic, attractive interactions<sup>8</sup>. In these systems the gel is a consequence of a phase transition, whereas in the work of Ruzicka *et al.*<sup>6</sup> the gel precedes phase separation. Also, what is spectacularly different in the scenario observed by these authors is the very dilute nature of the liquid, which is at least an order of magnitude less dense than the liquid state observed in isotropic colloids. The scenario is comparable to recent predictions from computer simulation models of patchy spherical particles<sup>1</sup> (Fig. 2a). Such model systems, which are known to display gas–liquid coexistence, show that the density of the liquid decreases on reduction of the

number of patches — that is, the valence. When the valence number approaches two, which can be achieved with mixtures of particles having either two or three sticky spots, the coexisting liquid density vanishes, whence comes the term ‘empty liquid’.

The experimental observations on Laponite are consistent with the predicted scenario. To demonstrate this, the authors provide additional computer simulations of disks decorated with five sticky patches, three on the rim and one at the centre of each face (Fig. 2b). The patches represent positively and negatively charged groups on the surfaces of the clay particles. Patches on the rim may stick to those on the faces, but face and rim spots are, for simplicity, assumed not to interact with their own kind. The model is further simplified by using a square-well potential for the face–rim attractive interactions. (Interestingly,



**Figure 1** | Phase diagram of diluted Laponite suspensions<sup>6</sup>. At long times,  $t_w$ , and depending on concentration,  $C$ , Laponite suspensions in water reach different states: coexisting clay-poor and clay-rich phases; equilibrium gel; and Wigner glass. The cartoons show the microscopic structures as seen in the computer simulations. The turbidity in the leftmost test tube indicates phase separation into clay-poor and clay-rich phases. Concentrations are shown as percentages in Laponite weight.



**Figure 2** | Models of patchy colloids. **a**, Models with  $M$  attractive patches equidistantly located on the surface of a sphere<sup>1</sup>. **b**, Patchy disk model for Laponite as studied by Ruzicka and colleagues<sup>6</sup>. The patches on the disk represent charges, three positive (red) at the rim and two negative (blue), one at the centre of each disk face. Positive and negative charges induce a directional face–rim attraction, and electrostatic repulsions limit the number of bonds per disk. Panel **a** reproduced with permission from ref. 1, © 2006 APS.

a similar model was used in ref. 9, but those authors apparently looked at lower volume fractions.) Notwithstanding the approximations in the model, the topology of the phase diagram resulting from the simulations is qualitatively consistent with the experiments. Similarly, the time evolution of the static structure factors from simulation and experiments agree.

All in all, Laponite suspensions are found to undergo a classical gas–liquid phase separation in which the liquid can either be an empty liquid or an equilibrium gel. It is important to note that empty liquids are not actually observed, but that their existence is inferred from the global scenario. In fact, an equilibrium gel can

be interpreted as an arrested empty liquid: both are network structures subject to continuous rearrangements driven by thermal fluctuations. In the case of the gel, however, bonds are stronger and rearrangements therefore are significantly (in fact drastically) less frequent. At higher Laponite concentrations the authors observe a Wigner glass<sup>6</sup> — a glass of clusters interacting with repulsive electrostatic interactions (Fig. 1) — but this is probably not the thermodynamically stable structure at these higher densities; which structure this is remains an open question.

The work by Ruzicka *et al.*<sup>6</sup> shines light on the remarkable properties of

clay, which finds applications in areas as diverse as slide analysis, oil drilling and the production of ceramics<sup>7</sup>. But what is more exciting, if colloids with sticky patches can be synthesized in a systematic way, is that we expect new structures with amazing properties to be found. In biological systems, for instance, intricate structures such as spherical and cylindrical virus capsids are thought to arise in large part because of sticky (for example hydrophobic) patches on the protein molecules that make up these structures. Empty liquids and equilibrium gels thus represent a wonderful sneak preview of what can be expected from patchy colloidal particles. □

Willem K. Kegels and Henk N. W. Lekkerkerker are at the Van't Hoff Laboratory, Debye Institute for Nanomaterials Science, Department of Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands.

e-mail: w.k.kegels@uu.nl; h.n.w.lekkerkerker@uu.nl

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## ORGANIC ELECTRONICS

# Harvesting randomness

The practical use of electronic ratchets has long been hampered by low output powers and cryogenic operating temperatures. A pentacene-based organic ratchet can now drive electronic circuitry at room temperature.

Peter Hänggi

Humans have always dreamt of machines that perpetually perform useful work from random fluctuations, such as those in ambient thermal noise. However, the second law of thermodynamics forbids the realization of such devices — it is indeed impossible to obtain useful work from a system held at fixed temperature without driving it out of thermodynamic equilibrium. Although single, rare events can extract energy from a system at equilibrium — in what may seem a violation of the second law — the extraction of net work on average (that is, over a period of time larger than the duration of a single event) is ruled out. This constraint is closely related to the concept

of a Maxwell demon<sup>1,2</sup>, which was originally introduced to pick a hole in the second law. To overcome the limitations of the second law, it is necessary to drive a system out of thermodynamic equilibrium.

At the microscale, where thermally driven random forces can dominate interparticle interactions, it has recently become possible to build out-of-equilibrium, bio-inspired nanomachines that perform work by harvesting environmental randomness<sup>3</sup>. Such machines are known as Brownian motors<sup>3</sup>, among which electronic ratchets<sup>4,5</sup> are prominent examples. Ratchet devices are set-ups composed of periodically arranged units with inherent asymmetry, and can be driven

by unbiased, time-dependent, random or deterministic forces. Electronic ratchets have so far been limited by the need for cryogenic operating temperatures, and by low output voltages and currents<sup>4,5</sup>. Thus they have been of limited practical use. In *Nature Materials*, Martijn Kemerink and collaborators<sup>6</sup> report an ingeniously designed organic electronic ratchet that operates up to radiofrequencies at room temperature and delivers an unexpectedly high output performance, sufficient to power a simple logic circuit.

As in a self-winding wristwatch, which works especially well on a gesticulating wearer, the working principle of any ratchet device is based on the clever combination of