

of site-selective 'spin labelling' in electron paramagnetic resonance<sup>9</sup>. Also, PHIP could be used for determining the functional mechanism of enzymes, for instance in dehydrogenase, by selective polarization of intermediates. The prospects are even brighter considering that the hardware needed to implement PHIP methods is now becoming commercially available.

Despite the diversity of its many possible applications, PHIP has limitations. So far, only a handful of chemical substances have proved amenable to PHIP studies, as the molecules to be polarized must contain an unsaturated moiety. Adams *et al.*<sup>3</sup> have substantially increased the number of systems by demonstrating that hyperpolarization can also be achieved without a 'proper' chemical reaction. That is, the temporary association of parahydrogen and a substrate on a transition-metal-based catalyst is sufficient to transfer the polarization to the substrate<sup>3</sup>. This polarization experiment can be applied to a significantly larger set of molecules, as only a free electron pair is needed that can bind to the transition metal. Clearly, research in chemistry, in particular the development of suitable catalysts for PHIP, is required.

Another drawback, inherent to all hyperpolarization methods, is the limited lifetime of the hyperpolarized state, which is subject to longitudinal ( $T_1$ ) relaxation. In liquids, relaxation times typically range from seconds to a few minutes, at best. So far, PHIP experiments have mostly been performed in batch processes and the hyperpolarized sample had to be measured as quickly as possible to minimize signal losses. This shortcoming can be alleviated by storing the hyperpolarization in slowly relaxing states<sup>10</sup>. This approach is easy to implement in PHIP as parahydrogen already possesses the singlet symmetry required in such experiments. Another recent advance towards lifting the limitations associated with the short lifetimes of the hyperpolarized state is the development of a method for continuous delivery of parahydrogen through hollow-fibre membranes<sup>11</sup>, ensuring a continuous supply of molecules with hyperpolarized  $^1\text{H}$  and  $^{13}\text{C}$  nuclei for minutes and possibly hours.

The remarkable signal enhancement generated by hyperpolarization methods, in particular by PHIP, can boost NMR applications in many fields of the natural sciences and medicine. The work of

Theis *et al.*<sup>1</sup> demonstrates that the combination of physics and chemistry can push the field of hyperpolarized NMR forward. However, it is still an emerging field, and exploiting its potential remains an ongoing challenge. □

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## LIQUID-LIQUID TRANSITIONS

# Silicon *in silico*

Extensive numerical simulations provide evidence that the thermodynamic behaviour of supercooled silicon is similar to that proposed for supercooled water: a line of liquid-liquid transitions that ends at a critical point. In the case of silicon, however, the critical point occurs at negative pressures.

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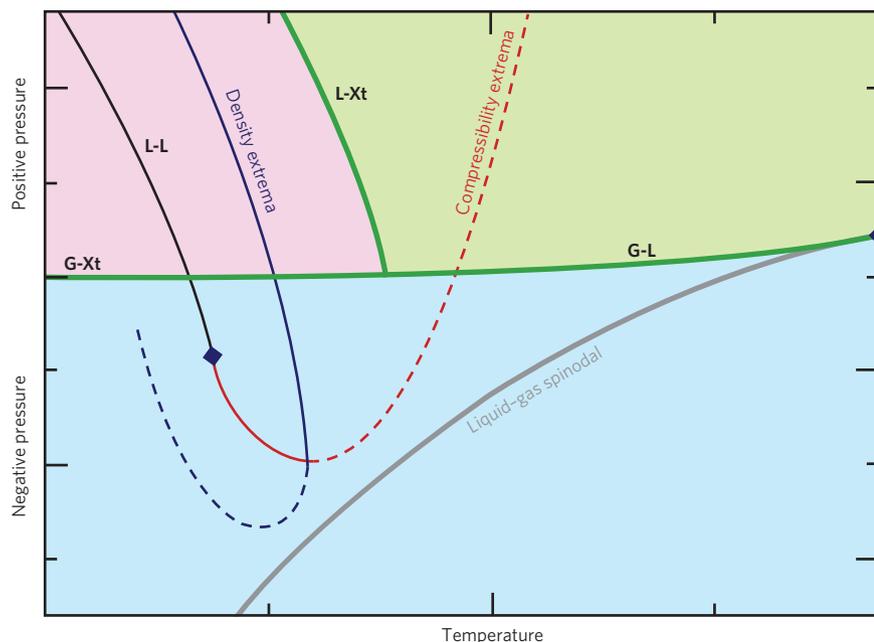
**S**ilicon is the second most abundant element after oxygen in the Earth's crust and the principal component of most semiconductor devices. In its pure form, it is commonly found as a polycrystalline or amorphous solid. On heating at ambient pressure, solid silicon melts into a liquid as most substances do. But, on cooling back, something different may happen. Simulations based on the Stillinger-Weber (SW) potential — a realistic classical model for silicon — suggested<sup>1</sup> that, if crystallization is avoided, the supercooled SW liquid undergoes at ambient pressure a first-order transition from a denser liquid to a network liquid with tetrahedral coordination, as originally predicted<sup>2</sup>. Writing in *Nature Physics*, Vishwas Vasisht and co-workers<sup>3</sup> now show — through extensive simulations — that this transition can be observed at different

pressures, defining a negatively sloped locus in the pressure-temperature plane that ends at negative pressures at a second-order critical point, where two distinct liquid structures of different density coexist.

We are all familiar with the possibility that a fluid separates into a low-density gas and a high-density liquid below a critical temperature. The interplay between entropy, which favours the disordered gas phase whereby each particle has the possibility of exploring the sample volume, and energy, which promotes the formation of a condensed phase in which nearest neighbour particles sit at the bonding distance, gives rise to the gas-liquid transition. What is less known is that certain liquids can in principle undergo further phase separation into two (or more<sup>4</sup>) distinct liquid phases, differing in their density and local structure. For this to

be possible, the liquid must be able to sustain two distinct environments of comparable thermodynamic weight.

In recent years, the possibility of a liquid-liquid (LL) transition in pure substances has been thoroughly investigated (mostly *in silico*) in several atomic and molecular fluids, including water, carbon, silicon, silica and germanium among others — substances that form a large fraction of our world and have fundamental biological and technological relevance. All of these substances are characterized by the formation in the liquid phase of open local structures, in which strong directional interactions, through stringent orientational constraints, control the geometry of the bonding pattern and the atomic or molecular coordination. These substances have a preference for tetrahedral coordination, whereby in the low-density



**Figure 1** | Phase diagram of SW silicon. The LL transition takes place in the region where the liquid (L, green) is metastable with respect to the crystal (Xt, pink, at positive pressure) or to the gas (G, light blue, at negative pressure). Blue diamonds mark the LL and the GL critical points. The red line indicates the position of minima (dashed) and maxima (full) in the  $T$  dependence of the isothermal compressibility, whereas the blue line indicates the locus of minima (dashed) and maxima (full) in the  $T$  dependence of the density, both along isobars. The line of compressibility extrema must meet the density extrema locus at its minimum before heading toward the LL critical point.

liquid phase the number of neighbours is not far from four, which is significantly smaller than the typical coordination number found in simple liquids, where the number of neighbours is approximately twelve owing to geometric (packing) reasons. An open local structure in which particles have well-defined relative orientations but strong bonding can indeed act as a candidate structure to compete with a more spherically symmetric environment in which bonds are more numerous but weaker and deformed. Such competition is a potential source for a LL critical point.

The first numerical evidence<sup>5</sup> of a LL transition dates back to 1992, when simulations of a classical model for water (the ST2 model) in supercooled states were analysed in search of the origin of the several thermodynamic anomalies that characterize this substance. For example, on varying the temperature  $T$ , liquid water presents a minimum in the isothermal compressibility and a maximum in the density. It took more than 15 years for computers to become sufficiently powerful to provide a clear picture of the complex scenario of interconnected anomalies<sup>6</sup> and definitive evidence for the existence, by means of an accurate study of the critical density fluctuations<sup>7</sup>, of the LL critical point

in ST2 water. The possibility of an analogous scenario for the case of supercooled silicon has long been discussed. The article by Vasishth *et al.*<sup>3</sup> finally resolves this issue, not only providing evidence that a second order critical point does exist, but also confirming the entire thermodynamic scenario expected in the presence of a LL critical point. A coherent complete thermodynamic view of supercooled SW liquid silicon is for the first time available (Fig. 1).

So far the existence of a liquid–liquid critical point in a pure bulk system has been proved only *in silico*, where the limited system size employed in numerical studies disfavors nucleation of the solid phase. Experimental studies are currently struggling to enter into the so-called no man's land, where spontaneous crystal formation prevents the observation of the metastable liquid. In the case of silicon, femtosecond pump–probe spectroscopy has been recently applied to follow the evolution of the structure over tenths of picoseconds on cooling after intense laser heating<sup>8</sup>. In the case of water, relevant progress may take place in studies in which the two amorphous solid forms, which have been interpreted as the glasses of the two liquids, are heated above their glass transition<sup>9</sup>. The difficulty in preventing crystallization is probably

intrinsic to the existence of the critical point. Indeed, a nearby LL critical point may promote crystallization, inducing density fluctuations matching the crystal density; a similar mechanism has been shown to be very valuable in the crystallization of short-range attractive colloids and proteins<sup>10</sup> for state points close to the standard gas–liquid critical point. Even if the critical point is technically located at negative pressure as in the SW case, its effect can be felt in a critical region that can extend up to ambient pressure and beyond.

The authors' work also raises provocative questions about the nature of atomic mobility in silicon and the nature of the glasses generated by the high- and low-density liquids. Interestingly, the same group has recently shown that varying the angle of the SW potential far from the tetrahedral value<sup>11</sup> results in the formation of a gel state, a very open structure of chains of two coordinated particles interconnected by a small number of branching points. This creative modification of the potential has a strong conceptual impact on our classification of the amorphous structure of silicon (and of all other tetrahedral systems), as it reinforces the hypothesis that arrested network-forming liquids are indeed the atomic and molecular counterpart of colloidal equilibrium gels<sup>12</sup>. Consistently, the materials generated by dynamic arrest of the low- and high-density liquids on the two sides of the LL coexistence, in silicon as well as in water, should be perhaps best understood as an atomic glass in which arrest is mainly driven by packing (the high-density glass) and an atomic gel in which arrest is driven by the establishment of an open network of strong directional bonds (the low-density glass). □

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