

out their functions and adapt to the environmental demands of ageing, such as impaired energy metabolism. ■

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High-temperature superconductivity

Quantum salad dressing

Jan Zaanen

The mystery of how electrons in a high-temperature superconductor flow without resistance grows deeper. New pictures at the atomic scale reveal two electronic phases that — like oil and vinegar — do not easily mix.

According to quantum mechanics, when space is the same everywhere, a particle should be everywhere at the same time. In low-temperature metals and superconductors, this principle rules the waves of the quantum fluids formed by the electrons. Under such conditions, electronic fluids seem remarkably featureless and insensitive to imperfections in the material. For instance, in a conventional superconductor the structure of the crystal lattice must be severely messed up to get a noticeable response from the superconducting electrons. But the high-temperature superconductivity found in certain copper oxide compounds is different. Quantum physics is still in charge but the underlying quantum fluids do not behave like their low-temperature counterparts. On page 412 of this issue, Lang *et al.*¹ take a direct look at this electronic fluid at the nanometre scale, using scanning tunnelling microscopy (STM)². Instead of the implacable perfection of the conventional superconductor, they find it to be rather messy.

What does the fluid look like? Imagine pouring salad dressing (a mixture of oil and vinegar) on to a plate covered with spots of fat. The result is droplets of vinegar immersed in an oily matrix. If the vinegar were superconductor and the oily matrix were a mystery state of electronic matter called the pseudogap phase, the result would be similar to what Lang *et al.* saw. (The fatty spots represent imperfections in the crystal lattice of the superconductor.) Until now, all we've been able to see at the macroscopic scale is the superconducting droplets merging together, as if the plate's contents as a whole turn into pure vinegar. This merging occurs because of a quantum effect called Josephson coupling. The nanoscale images obtained by Lang *et al.* help us probe beyond the macroscopic surface of this electron system.

Understanding the quantum behaviour of a single electron is hard enough, but there

are approximately 10^{23} strongly interacting electrons in every gram of earthly matter. Fortunately the basic rules simplify when the system becomes big. The secret of conventional quantum fluids is that the particles seem to forget that they interact when the system size is scaled up. But they keep their quantum-mechanical habit of spreading out across all the space, and their quantum-statistical nature: fermions (electrons) turn into a Fermi gas (normal metals), and bosons (pairs of electrons) turn into a Bose–Einstein condensate (superconductors).

This is what lies behind the implacable perfection of conventional quantum fluids: the system of particles inherits its basic properties directly from its constituents. But condensed-matter physics is increasingly concerned with quantum systems that do not conform to this description — such as the electron system of the high-temperature superconductors. Despite unprecedented research activity (approximately 100,000 papers since its discovery in 1987), high-temperature superconductivity seems as mysterious as ever. Part of its continuing fascination for physicists is its potential to reveal fundamental insights into the collective behaviour of quantum particles^{3,4}.

I've already given away the punch-line of Lang and colleagues' result¹: the electron system of their superconductor looks like salad dressing. But there is deeper meaning to this kitchen-table metaphor — the STM pictures are messy because the superconducting electrons do not forget their interactions when they turn into a quantum fluid. Instead, the electronic matter is still strongly interacting, causing it to act in a highly collective way. Such collective behaviour carries its own logic that supersedes even the differences between classical and quantum physics, allowing me to use everyday phenomena to describe what is happening.

To explain further, salad dressing starts

out as protons, neutrons and electrons. If these were non-interacting, salad dressing would remain featureless. Instead, these entities bind into lipid, acetic acid and water molecules, which in turn form two strongly interacting, immiscible fluids: vinegar and oil. Something similar happens in the high-temperature superconductors. In the beginning there are electrons and some crystal-lattice vibrations. These are strongly interacting and the electrons quickly lose their identity and morph into a collective phase with its own emergent properties. Apparently, there are two of these phases — the 'superconducting' and the 'pseudogap' phases — but they do not easily mix. This highly collective electron matter reacts strongly to imperfections in the superconductor (probably missing oxygen atoms in the crystal lattice), causing the droplet picture.

The superconducting phase shares at least some properties with a conventional superconductor, but the pseudogap phase is still a mystery. There are several reasons why it could exist. Initially the pseudogap phase was thought to correspond to a high-temperature precursor of the superconducting state, in which the electrons formed pairs that did not undergo Bose–Einstein condensation until the temperatures dropped low enough². More recently it was thought to be a novel quantum state of matter characterized by an exotic form of order that is difficult to observe experimentally (hidden order)⁴. Theorists came up with several ingenious proposals regarding the nature of this order, such as the flux and *d*-density wave orders^{5,6}. Lang *et al.*'s observation of a two-phase mixture at low temperatures makes the high-temperature-precursor explanation less likely, as the pseudogap phase can exist simultaneously with the superconducting state. But it does give strong support to the notion that the pseudogap phase is a separate state of matter.

Lang *et al.* also discovered a very strange property of the pseudogap phase. To investigate the differences between the two phases they introduced nickel impurities into some of their samples. These impurities produce STM fingerprints in the superconducting phase known as 'impurity resonances'. According to theory, the authors should have found a similar, but modified, pattern of impurity resonances in the pseudogap regions. Instead, their measurements show that the resonances disappear completely. This is a serious challenge for existing theories, which are invariably based on the assumption that both phases are very similar on atomic scales, with differences emerging only on larger scales. So if the impurity resonances look drastically different in the pseudogap and superconducting phase, the phases must be dissimilar at the atomic scale. Again the salad-dressing metaphor is helpful — it seems that only a few

electrons are needed to form distinguishable oil (pseudogap) and vinegar (superconductivity) 'molecules'.

What good might come of all this? Studies like these are revealing amazing diversity in the behaviour of these mystery electron systems at the nanoscale. Indeed, much more appears to be going on than in more conventional systems, such as gold, silicon and carbon nanotubes, which form the building blocks of current nanotechnology. Perhaps one day the rich electronic nano-life of high-temperature superconductors will

also be tamed and exploited. We are not just solving a mystery, but witnessing the birth of a new frontier of nanoscience. ■

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Nitrogen cycle

Natural organic tendency

Nico van Breemen

Dissolved nitrogen is usually thought to be transported from land to sea in inorganic form. But the predominance of organic nitrogen in streams in temperate South America suggests that this view needs a rethink.

The Haber–Bosch process for transforming atmospheric N_2 into ammonia, and so creating nitrogen fertilizer, was invented almost a century ago. Nitrogen is the main nutrient that plants take up from soils, so the Haber–Bosch process was in large part responsible for the vast increase in food production that helped to support a booming human population during the twentieth century. But it has also dramatically altered the global nitrogen cycle. The latest research attesting to that point, by Perakis and Hedin¹, appears on page 416 of this issue.

In ecosystems that have been subject to intensive human activity, such as the temperate Northern Hemisphere, nitrogen that leaches from ecosystems is largely in inorganic form (nitrate). But Perakis and Hedin find that in temperate parts of Chile and Argentina, which have remained free of such human intervention, the nitrogen is mainly organic in form. It seems, then, that our tendency to carry out research in northern regions has given us a misleading picture.

Over the past hundred years, human activity has doubled nitrogen input into the global terrestrial nitrogen cycle. In consequence, in heavily industrialized and densely populated areas we have polluted the atmosphere with ammonia and nitrogen oxides; increased atmospheric deposition of nitrogen; acidified soils, streams and lakes; decreased biodiversity by affecting plants adapted to the efficient use of nitrogen; and affected coastal marine fisheries². These consequences have prompted research into many aspects of the nitrogen cycle, and the results have provided fairly detailed nitrogen budgets for intensively studied areas in the Northern Hemisphere³. Such budgets differ greatly from those that might apply in the areas studied by Perakis and Hedin¹,

quantitatively as well as qualitatively (Fig. 1).

A central feature of nitrogen budgets is the formation of nitrate by a series of biological processes, starting with the decomposition of organic nitrogen in plant litter to ammonium. Ammonium is partly taken up again by plants and partly oxidized by bacteria to nitrate. Nitrate that is not taken up by plants is either leached into rivers or reduced by denitrifying bacteria, mainly to atmospheric N_2 . Denitrification closes the

nitrogen cycle, which started with biological or industrial fixation of N_2 to forms that are available to plants and microbes (most of which cannot use N_2).

The nitrogen cycle is intimately linked to the carbon cycle. Biogeochemical models that describe transformations of either cycle on regional to global scales feature inorganic nitrogen as the dominant feature of nitrogen cycling. These models are commonly used to describe the effects of global change^{4–6}, including those that bear on the question of how much carbon is sequestered on land in response to increased CO_2 in the atmosphere⁷.

Perakis and Hedin¹ repeatedly sampled and analysed stream water in parts of Chile and Argentina (see the map on page 417). They selected one hundred streams, in unpolluted and often remote forested watersheds, looking at ecosystems at different stages of development and subject to a broad range of climatic and geological conditions. They found much more dissolved organic nitrogen than nitrate nitrogen in their water samples, in contrast to a dominance of nitrate in the streams of northern temperate forests (Fig. 1).

It is unlikely that differences in plants and microbes between the hemispheres cause these differences, so the observations call into question several standard concepts about the nitrogen cycle in undisturbed forest ecosystems. Is the dominance of dissolved nitrate, even in moderately polluted northern temperate forests, caused by increased atmospheric deposition there and logging? If it is, this effect has been overlooked by soil

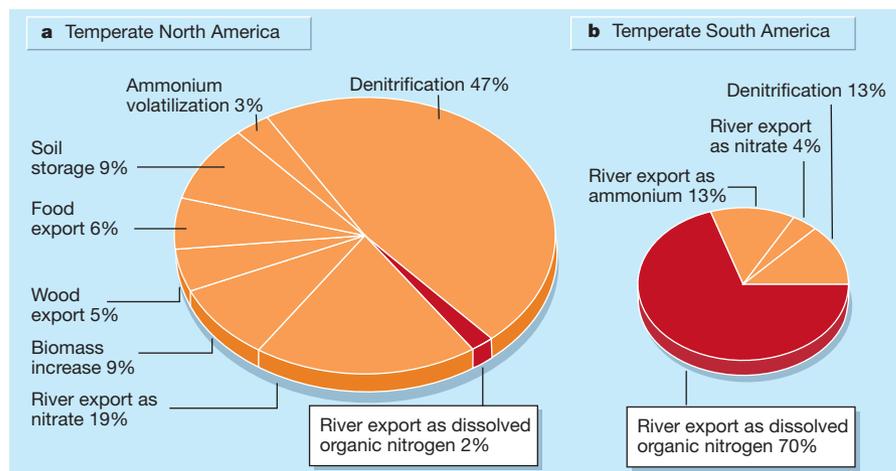


Figure 1 Forms of nitrogen storage in, or export from, two ecosystems in North and South America. a, Data for a largely forested region in the northeastern United States³. Here, nitrogen is found to be exported primarily in inorganic form. b, The pristine forest area in Argentina and Chile studied by Perakis and Hedin¹. Most notably, most of the nitrogen exported in streams and rivers here is in organic, rather than inorganic, form. The two regions have about the same annual precipitation of 1,100 mm. But the total 'sinks' in a are almost ten times those in b (about $36.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$ compared with $0.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$). The difference is due to a much greater input of nitrogen through human agency in the United States. As well as nitrogen export in water, and denitrification, sinks in the forested northeastern United States include export in agricultural and forestry products (food and wood); volatilization of ammonia from manure and fertilizers; storage in growing forests (biomass increase); and accumulation in soils, mainly in forests and in suburban land. The budget in b was estimated from the new data¹, with the assumptions that the nitrogen in soils and biomass is in steady state, and that the ratio of denitrification to nitrate export is the same in both regions.