QUANTUM MATERIALS

The expanding materials multiverse

Heat capacity and Raman experiments point to fractionalized excitations in a dipole liquid

By **Ben J. Powell**

High-energy physicists are limited to studying a single vacuum and its excitations, the particles of the standard model. For condensed-matter physicists, every new phase of matter brings a new "vacuum." Remarkably, the low-energy excitations of these new vacua can be very different from the individual electrons, protons, and neutrons that constitute the material. The materials multiverse contains universes where the particle-like excitations carry only a fraction of the elementary electronic charge (*1*), are magnetic monopoles (*2*), or are their own antiparticles (*3*). None of these properties have ever been observed in the particles found in free space. Often, emergent gauge fields accompany these "fractionalized" particles (*2*, *4*, *5*), just as electromagnetic gauge fields accompany charged particles. On page 1101 of this issue, Hassan *et al.* (*6*) provide a glimpse of the emergent behaviors of a putative new phase of matter, the dipole liquid. What particles live in this universe, and what new physics is found in this and neighboring parts of the multiverse?

Liquids and gases look the same everywhere, but the periodic arrays of atoms in crystals break translational and rotational symmetries. This broken symmetry leads directly to the important differences between a crystal and a fluid—for example, the crystal's rigidity (*7*). The differences between gases and liquids are more subtle. Particles move freely in a gas, like cars on the open road. In a liquid, the motion of particles is correlated—i.e., it depends on what other particles are doing, like city driving (see the figure). Continuing this analogy, a glass is like a traffic jam, and a crystal resembles a parking lot with every particle neatly in place.

Some phases of matter are easier to detect than others. In ferromagnets, the spins

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of unpaired electrons (radicals) align, creating a net magnetization (see the figure). This property allowed ancient civilizations to discover ferromagnetism. In antiferromagnets, neighboring spins point in opposite directions, leaving no net magnetic moment. Thus, antiferromagnetism was not observed until the 20th century. We still await conclusive experimental evidence for topological spin liquids—proposed phases where the spins lack long-range order but display long-range quantum correlations known as entanglement (*5*).

(Anti)ferroelectrics are phases in which electric dipoles align (anti)parallel to their nearest neighbors (see the figure). (Anti)ferromagnets and (anti)ferroelectrics could be described as spin crystals or dipole crystals, respectively, as a symmetry is broken. Simple paramagnets and paraelectrics, with little correlation between spins or dipoles, respectively, are essentially spin gases or dipole gases. Similarly, systems with strong correlations between spins or dipoles, but no broken symmetry, are known as spin liquids (*4*, *5*) and dipole liquids (*6*, *8*, *9*).

Hassan *et al.* exploited two special features of molecular crystals: their internal structure and the dipole inherent in dimer Mott insulators. They studied salts of bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF). In the dimer Mott phase, most (BEDT-TTF)$_2$ dimers carry a charge of +1. They are insulating because excitations that increase the charge of one dimer are bound to excitations that decrease the charge on a nearby dimer. Classically, the positive charge on a dimer must reside on one molecule or other, so there are two states that differ by the flip of an electric dipole. Quantum tunneling can occur between these states, as in the Creutz-Taube ion (*10*). If the tunneling is sufficiently rapid, the two states are in a quantum superposition, and a dipole gas forms.

Hassan *et al.* used Raman scattering to probe the two vibrational modes of the molecules: one mode that is sensitive to the charge on the molecule and another that is not. This difference allowed them to study dipolar fluctuations. κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl is a dipole solid at low temperature (T), spontaneously breaking the inversion symmetry of the (BEDT-TTF)$_2^+$ dimers. However, in κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Br, the dipoles fluctuate rapidly, leading to a dipole fluid. The observation of a low-energy continuum of excitations in the Raman spectrum is consistent with the formation of a dipole liquid with fractionalized excitations.

The low-temperature heat capacity of the dipole solid in κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl is proportional to T^3, as one would expect from phonons or other bosonic excitations. However, in κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Br, there is an additional term in the heat capacity proportional to T. Itinerant fermionic excitations would be a natural explanation of this term.

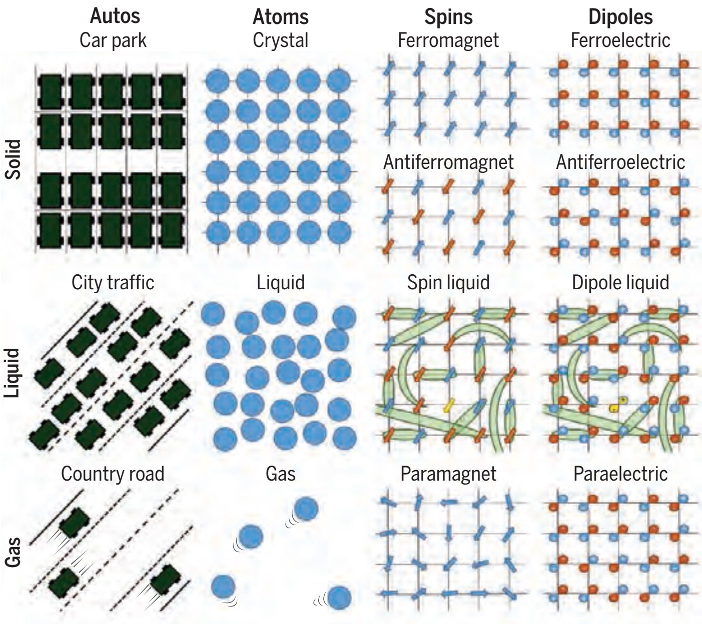
Hassan *et al.* argued that these two experiments are evidence for either collective excitations of the dipoles or hybrid spin-dipole excitations driven by interactions between the dipoles and the unpaired spins of the (BEDT-TTF)$_2^+$ radicals. In a broken symmetry phase, such as a dipole solid, the collective excitations are Goldstone bosons (*7*). However, in a dipole liquid, excitations might fractionalize into fermionic particles, as appears to happen in some spin liquids (*4*, *5*). A possible route to liquid phases is sketched in the figure. Pairs of spins (or dipoles) form singlets. Within each singlet the spins (dipoles) point in opposite directions, but both spins (dipoles) can flip simultaneously. This is an example of quantum entanglement. A quantum state composed of many different configurations of spin singlets can produce a spin liquid (*4*, *5*). Excitations in such a state, called spinons, involve unpaired spins moving about the crystal and can obey either Fermi or Bose statistics (*4*, *5*). Can something similar happen in a dipole liquid?

If the excitations have hybrid spin-dipole character, might spin-dipole interactions also drive the exotic physics of the BEDT-TTF salts? Little is known about the spin physics in κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Br, so Hassan *et al.* turned to κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, which is believed to be a spin liquid (*4*). No dipole liquids or solids were seen in this material, so its physics likely arises solely from spins.

Like many of the most interesting experiments, the work of Hassan *et al.* contains more questions than answers. They have discovered an exciting new universe ripe for exploration. The conclusive demonstration that the excitations to its "vacuum" are itinerant fermions may require new experimental tools that can directly probe the particle-like excitations. BEDT-TTF salts often become superconducting under pressure (*4*), and many physicists believe that this superconductivity results from the material failing to become a spin liquid, despite its propensity to do so (*11*). Do failed dipole liquids also superconduct? How common are dipole liquids? There is evidence for one in BaFe$_{12}$O$_{19}$ (*8*) and proposals for building them from polar molecules (*9*). Might the exotic behaviors of ice X (*12*) be understood as a quantum dipole liquid? ■

A motor tour of the multiverse

Solid, liquid, and gas phases of particles, spins, and dipoles, along with their automotive analogs, are shown. The sketch for the dipole liquid is speculative. Hassan *et al.*'s work suggests that dipole liquids are similar to spin liquids and may support itinerant fermionic quasiparticles.



For the spin and dipole liquids, the green ribbons indicate quantum correlations between spins or dipoles pointing in opposite directions. Spinons, excitations in spin liquids that are quantum superpositions of unpaired spins, are highlighted in yellow.

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