Negative Temperatures?

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PHYSICS

Negative Temperatures?

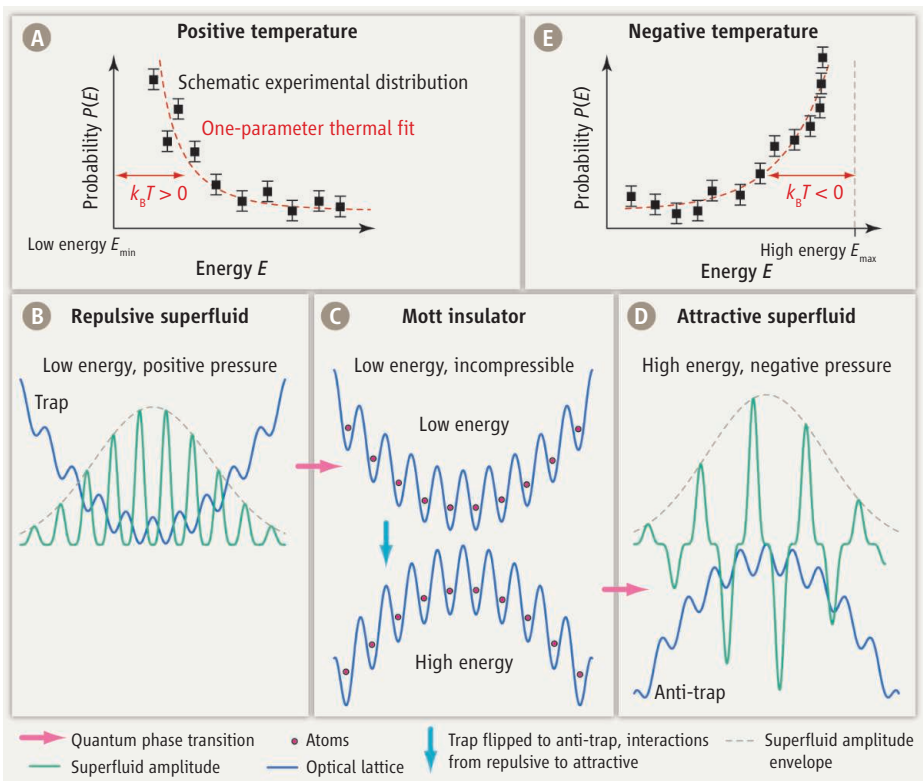
A cloud of potassium atoms is tuned to negative temperatures via a quantum phase transition.

Lincoln D. Carr

Ultracold quantum gases present an exquisitely tunable quantum system. Applications include precision measurement (*1*), quantum simulations for advanced materials design (*2*), and new regimes of chemistry (*3*). Typically trapped in a combination of magnetic fields and laser beams, strongly isolated from the environment in an ultrahigh vacuum, and cooled to temperatures less than a microdegree above absolute zero, they are the coldest known material in the universe. The interactions between atoms in the gas can be tuned over seven orders of magnitude and from repulsive to attractive (*4*). The addition of standing waves made from interfering lasers at optical wavelengths gives rise to an optical lattice, a crystal of light, periodic just like the usual crystals made of matter. On page 52 of this issue, Braun *et al*. (*5*) use these special features of ultracold quantum gases to produce a thermodynamic oddity—negative temperature.

Temperature is casually associated with hot and cold. How can something be "colder" than absolute zero? The answer lies in a more precise notion of temperature. Temperature is a single-parameter curve fit to a probability distribution. Given a large number of particles, we can say each of them has a probability to have some energy, $P(E)$. Most will be in low-energy states and a few in higher-energy states. This probability distribution can be fit very well with an exponential falling away to zero. Of course, the actual distribution may be very noisy, but an exponential fit is still a good approximation (see the figure, panel A). Negative temperature means most particles are in a high-energy state, with a few in a low-energy state, so that the exponential rises instead of falls (see the figure, panel E).

To create negative temperature, Braun *et al*. had to produce an upper bound in energy, so particles could pile up in high-energy rather than low-energy states. In their experiment, there are three important kinds of energy: kinetic energy, or the energy of motion in the optical lattice; potential energy, due to magnetic fields trapping the gas; and interaction energy, due to interactions between the atoms in their gas. The lattice naturally gives an upper bound to kinetic energy via the formation of a band gap, a sort of energetic barrier to higher-energy states. The potential energy was made negative by the clever use of an anti-trap on top of the lattice, taking the shape of an upside-down parabola. Finally, the interactions were tuned to be attractive (negative). Thus, all three energies had an upper bound and, in principle, the atoms could pile up in high-energy states.



Less than zero. (**A**) Temperature is a one-parameter fit: As the energy gets large, the probability that an atom will have that energy falls away exponentially. A quantum phase transition from a repulsive superfluid (**B**) to a Mott insulator (**C**) provides a bridge to an attractive superfluid (**D**), resulting in negative pressure balanced by negative temperature (**E**).

Braun *et al*. convinced their gas to undergo such a strange inversion using a quantum phase transition (*6*), an extension of the well-known thermodynamic concept of phase transitions to a regime in which the temperature is so low that it plays no role in the change of phase. In this case, they worked with two phases, superfluid and Mott insulator. In a superfluid, the gas flows freely without viscosity and is coherent, like a laser, but made of matter instead of light. In a Mott insulator, the atoms freeze into a regular pattern and become incompressible, similar to a solid. Braun *et al*. first make their atoms repulsive in a superfluid phase. They tune them to a Mott insulating phase by simply turning up the intensity of the optical lattice lasers, making the lattice deeper. Then they tune the interactions to be attractive and at the same time turn their trap upside down to be an anti-trap. Finally, they melt the Mott insulator to obtain an attractive superfluid. These anti-traps have been used before, to create a self-propagating pulse of atoms that does not disperse (a bright soliton) from attractive gases in one dimension (*7*, *8*). However, attractive quantum gases in two and three dimensions can implode, rather spectacularly (*9*). This tendency to implode is called negative pressure. The negative temperature is precisely what stabilizes the gas against negative pressure and implosion; the Mott insulator serves as a bridge state between positive temperature and pressure, and negative temperature and pressure (see the figure, panels B to D).

Braun *et al*.'s exploration of negative

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temperature is part of a general theme of pushing the limits of thermodynamics and quantum mechanics with ultracold quantum gases. Quantum phase transitions have been explored intimately in these systems (*2*, *10*). There is a special class of dynamical systems, called integrable, that never truly develop a temperature because their properties are different from those of a system in equilibrium with a thermal environment. Classically, integrability is opposed to chaos; chaotic dynamical systems thermalize and become thermodynamic. The borderline between integrability and chaos is described by a famous and beautiful theory, called Kolmogorov-Arnold-Moser (KAM) theory (*11*). To date, we do not know whether there is a KAM theory for quantum mechanics. It is now believed that a whole new concept is needed to deal with near-integrable quantum systems, casually called prethermalization, in which physical quantities after relaxation are described by the fancy name "generalized Gibbs ensemble" (*12*–*15*).

Thermodynamics is at the heart of chemistry, engineering, and many biological questions. In ultracold quantum gases, the basic concepts of thermodynamics, positive or negative temperature, or whether a temperature concept is even relevant, are under intense and profound exploration.

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CHEMISTRY

Bioinspired Oxidation Catalysts

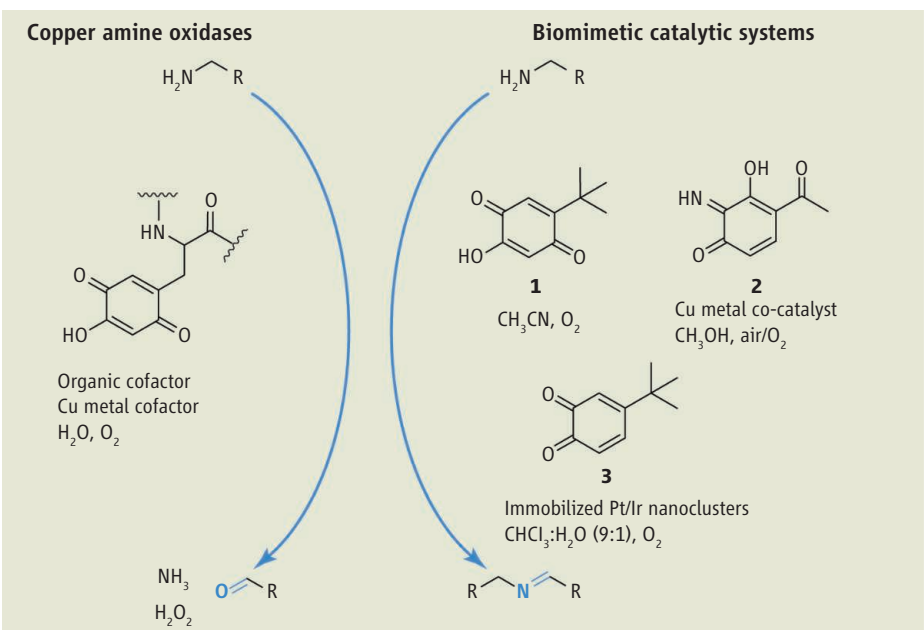
Metalloenzyme-like catalytic systems oxidize amines to imines under environmentally friendly conditions.

Martine Largeron and Maurice-Bernard Fleury

Imines are key intermediates in the synthesis of fine chemicals and numerous biologically active compounds. They have traditionally been prepared through condensation of amines with carbonyl compounds, but the latter are extremely active and thus difficult to handle. A powerful alternative strategy involves coupling primary alcohols and amines through catalytic alcohol activation by temporary oxidation to an aldehyde (*1*). However, with few exceptions (*2*), these aerobic oxidative reactions require high reaction temperatures and catalysts that contain expensive and rare metals. Furthermore, this approach is challenging because imines can readily undergo hydrogenation (*3*). Recently developed metalloenzyme-like catalytic systems allow the aerobic oxidation of amines to imines under very mild conditions. They are environmentally friendly because they avoid the use of oxidants, energy-consuming processing steps, and undesirable reaction media.

Efficient catalytic methods exist for the oxidation of secondary amines ($R^1CH_2NHR^2$) to imines ($R^1CH{=}NR^2$) (*4*), but until recently, little attention was given to the oxidation of primary amines (RCH_2NH_2), probably because the generated imines (RCH=NH, in which a second α-amino hydrogen is available) are generally intermediate products that are rapidly dehydrogenated to nitriles (RC≡N) (*5*). Green processes have also been developed that use biocompatible transition-metal catalysts, with dioxygen or air as the sole oxidant. However, most of these methods have limitations. For example, a solvent-free copper-catalyzed synthesis of imines from primary amines uses air as a benign oxidant but requires high reaction temperatures (*6*). A simple copper/TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) system catalyzes the aerobic oxidation of amines to imines at room temperature, but is efficient only for benzylic amines (*7*).

Naturally occurring metalloenzymes have long been recognized as attractive catalysts for aerobic oxidations because they can operate under mild conditions with complete che-



Biomimetic success. (Left) Copper amine oxidase enzymes catalyze the formation of aldehydes from amines. (Right) Catalyst systems developed to mimic these natural enzymes enable the aerobic oxidation of amines to imines under mild conditions.

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