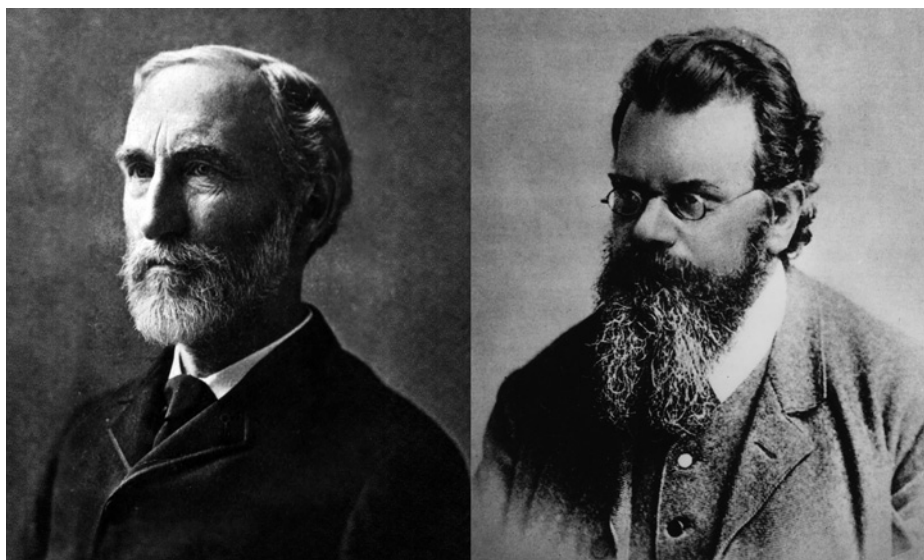THERMODYNAMICS

Not hotter than hot

A careful revision of the rudiments of statistical physics shows that negative temperatures are artefacts of Boltzmann's approximate definition of entropy. Gibbs' version, however, forbids negative absolute temperatures and is consistent with thermodynamics.

Igor M. Sokolov

From time to time, it is good to look back and reflect on the very foundations of science. Something that is now textbook material was usually once a topic of debate, and a generally accepted solution might still turn out to be incorrect. Writing in *Nature Physics*[1], Jörn Dunkel and Stefan Hilbert have revisited the concepts of temperature and entropy — a timely rethink in the light of some beautiful recent experiments involving negative temperature states in ultracold quantum gases that are trapped in optical lattices[2,3].

Negative temperature states were first observed[4] in nuclear spin systems by Edward Purcell and Robert Pound in 1951, and the implications of negative temperatures were discussed[5] by Norman Ramsey in 1956. Negative temperatures arise in situations where the high-energy states of a system are occupied more strongly than its low-energy states. The temperature T can be defined by fitting the occupation probabilities p_i, which are proportional to the Boltzmann factors $\exp(-E_i/k_B T)$, where E_i is the energy of state i. The negative temperature states of the system have higher energies than those associated with positive temperatures. Thus, the temperature scale runs $+0$ K,…, $+300$ K,…, $+\infty$ K, $-\infty$ K,…, -300 K,…, -0 K (ref. 5); systems at negative temperature are hotter than systems at positive temperature[4] — they are 'hotter than hot'.

The important question now addressed by Dunkel and Hilbert[1] is whether the fit parameter $T = T_B$ (where the subscript 'B' stands for Boltzmann) corresponds to the usual thermodynamic interpretation of temperature. In thermodynamics, temperature is a derived quantity, the two primary properties being the system's energy and entropy. If the dependence of entropy S on energy E is known, the system's temperature is obtained simply as the inverse of the derivative of $S(E)$ with respect to E. The axiomatic framework of thermodynamics — founded on an enormous number of observations, and checked through application to a multitude

of systems — is extremely solid, and has a clear mathematical structure based on the theory of differential forms.

To connect the thermodynamic properties of a system to its atomistic structure, one has to resort to statistical physics, pioneered by Josiah Willard Gibbs and Ludwig Boltzmann more than a century ago. Statistical mechanics has its own concept of entropy, or rather, several related concepts, which are 'surrogates' of the thermodynamic entropy. The idea is to look for a mathematical quantity that is connected with the equations governing the collective dynamics of the system's particles and complies with the axioms of thermodynamics. This 'mathematical entropy' can fulfil these axioms exactly or only approximately, with the corresponding approximation becoming exact in some limiting cases.

The entropy of statistical mechanics has to do with counting the possible states of a system. In a quantum system with a

discrete energy spectrum, one simply counts all possible states with energies in some prescribed interval. If the number of states is W, the entropy is given by Boltzmann's famous formula $S = k_B \ln W$. For isolated systems, the standard (textbook) approach is to take some energy interval ΔE around the actual energy E of the system (which for macroscopic systems can never be measured exactly anyway) and count the states within it. Gibbs' proposal was instead to count all states with energies lower than E. Dunkel and Hilbert[1] call these definitions the Boltzmann entropy and the Gibbs entropy, respectively, and show that it was Gibbs who proposed the correct way of 'counting': it is the Gibbs entropy that exactly matches the mathematical structure of thermodynamics, whereas Boltzmann's is only an approximation. The temperature, calculated from the functional dependence of the entropy on the energy as stated above, will be different for both definitions.

Figure 1 | Gibbs versus Boltzmann. In counting microstates to measure the entropy of a system, Gibbs (left) had a different prescription to that of Boltzmann (right). Although Boltzmann's approach can seemingly result in negative absolute temperatures, Dunkel and Hilbert[1] have proved that the correct thermodynamic treatment, following Gibbs, causes no such problems.

For typical macroscopic systems, the difference between the two procedures (as well as the exact value of the width of ΔE in Boltzmann's approach) does not play any role: the number of states grows so fast with the system's energy that almost all states that should be included in the count are concentrated around E. The difference becomes important, however, when the energy of the system is bounded from above, as it is in Purcell and Pound's nuclear spin system[4] or in a quantum gas[2] displaying energy gaps. In this case, the number of states within an interval ΔE (and thus the Boltzmann entropy) decays as a function of E, and the temperature associated with Boltzmann's prescription (which is the same as the fitting parameter T_B) can become negative.

The overall number of states below E cannot decay, however: the Gibbs entropy is a non-decaying function of the energy, and

the Gibbs temperature T_G (which coincides with the thermodynamic one) remains positive. On the Gibbs temperature scale, the whole domain of negative Boltzmann temperatures corresponds to the limiting case $T_G \to \infty$: such systems are hot, but not hotter than hot. The two temperatures T_G and T_B are connected to each other through a simple equation involving the heat capacity of the system, and that equation reveals the conditions under which the difference between the two temperatures can be neglected[1].

Negative ~~absolute~~ temperatures are neither bad nor wrong, as long as one doesn't forget what one is talking about. Failing to remember that the Boltzmann temperature is not the thermodynamic temperature can cause problems. From the point of view of pure logic, it could be that thermodynamics is faulty, and that the Boltzmann temperature is the 'real' one.

However, using negative temperatures with the formalism of thermodynamics (which, as we have now seen, forbids them) is inconsistent anyway. The incorrect use of negative (Boltzmann) temperatures — such as inserting a negative temperature into the Carnot formula for the efficiency of a heat engine, giving an efficiency exceeding unity — simply doesn't work. ❑

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SPECTROSCOPY

Combs grow bigger teeth

A combination of two Nobel ideas circumvents the trade-off between power and accuracy in ultraviolet spectroscopy.

Scott A. Diddams

From its beginnings in the experiments of Joseph Fraunhofer to the most recent laser-based measurements with uncertainty at the 10^{-17} level[1,2], spectroscopy has been a fantastically successful tool for unravelling the structure and workings of atomic and molecular systems. Indeed, optical spectroscopy progressed hand-in-hand with the birth of quantum mechanics in the 1900s. And the invention of the laser around 1960 provided a more precise spectroscopic tool, which not only enabled exquisite probing of atomic structure, but was also critical for

spectroscopy-based cooling and trapping of atoms.

With such a storied past, one might wonder what worthwhile spectroscopic advances could help reveal still further details of our physical world? An outstanding challenge in laser spectroscopy is the precise measurement of transitions in the vacuum ultraviolet (VUV) region of the optical spectrum — wavelengths between approximately 10 and 200 nm. Of particular interest are small atomic and molecular species such as hydrogen and helium and their ionic and more exotic counterparts,

antihydrogen or antiprotonic helium, for example[3–5]. The relative simplicity of these atoms makes their energy structure amenable to precise calculations based on quantum electrodynamics, which can then be compared with spectroscopic measurements. Another noteworthy VUV spectroscopic problem is the direct observation of the low-lying nuclear transition in thorium-229, which is predicted to be near 160 nm. This rare optical transition could serve as a unique window into the nucleus, as well as a reference for a nuclear clock[6] with an exceptional quality factor and uncertainty potentially approaching 10^{-20}.

However, it is at this point that a challenging measurement issue arises: there are no widely tunable narrow-linewidth lasers below about 180 nm that would be suitable for precision spectroscopy of these interesting species. And although nonlinear conversion techniques in gases can produce VUV laser radiation, these require high-energy pulsed lasers that lack the necessary spectral resolution. Thus, it seems that Fourier's uncertainty limit prevents the combination of high peak power from a short-pulsed laser needed to generate VUV light, and high spectral resolution from a continuously oscillating laser required to achieve the desired precision.
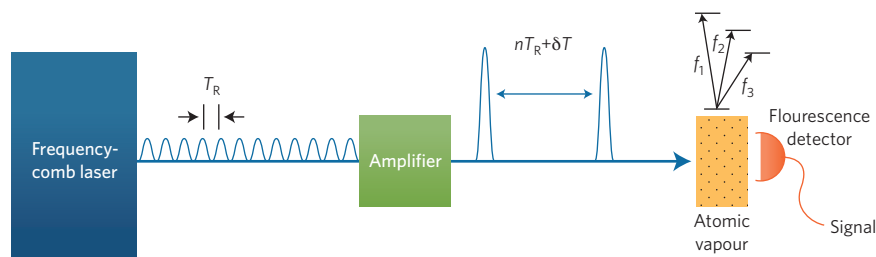
Figure 1 | Ramsey-comb spectroscopy. Morgenweg *et al.*[7] selectively amplified pairs of Ramsey pulses from a train, separated by a time T_R, generated by a frequency-comb laser. These pulses excited a mix of rubidium and caesium vapours. A time-domain analysis of the oscillating Ramsey signal as the time between the pulses varied (δT) provided simultaneous determination of the frequencies ($f_1, f_2, f_3...$) of the electronic transitions of the atoms.