

# The Meaning of Temperature

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The summer of 1988 found me working with a dozen high-school teachers on the subject "Atoms in Motion." One of our classes was devoted to "the meaning of temperature." The topic may seem simple, but it can be deceptive. Misconceptions are propagated in many textbooks, and there are several surprises. What follows is an expanded version of the notes I handed out following our class.

## The Essence

Among the many things that I learned from Professor Eric Rogers was a simple, clear meaning for temperature: temperature is hotness measured on some definite scale.<sup>1</sup> In turn, "hotness" is the tendency to transfer energy in irregular, microscopic fashion. (It is the tendency to transfer energy "as heat.")

We can order objects according to their hotness. A red-hot piece of iron is hotter than iron we can hold in our hands; it is not as hot as white-hot iron. If we place the three pieces in contact, as sketched in Fig. 1, then energy is transferred from "red hot" to "can be handled" and to "red hot" from "white hot." "Temperature" provides such an ordering on a convenient numerical scale. In our illustration, the temperatures might be these

$$T_{\text{can be handled}} = 300 \text{ K} \quad (1)$$

$$T_{\text{red hot}} = 1000 \text{ K} \quad (2)$$

$$T_{\text{white hot}} = 1700 \text{ K} \quad (3)$$

To say that object A is "hotter" than object B is to say that if A and B are placed together, then energy flows from A to B.

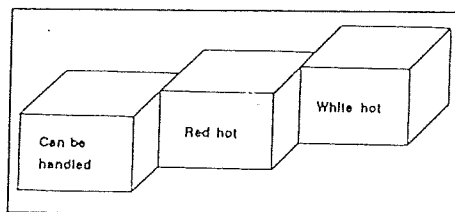


Fig. 1. Among the three objects, energy is transferred from right to left. That sequence provides an ordering of the objects according to their "hotness."

As time goes on, the rates of energy transfer between our blocks decrease toward zero. When the rates become zero, we have "thermal equilibrium." The three blocks now have equal hotnesses, that is, equal tendencies to transfer energy, which cancel out one another's effects. Equal

hotnesses imply equal temperatures. In short, mutual thermal equilibrium implies equality of temperatures and vice versa.

While correct, this presentation of what temperature means is austere and can leave one with a desire for a more intuitive grasp. The attempt to provide a more intuitive view, however, may lead to error, as we will see.

## A Common Misconception

For a dilute gas, the empirical gas law gives the pressure  $p$  as

$$p = \frac{N}{V} kT \quad (4)$$

where  $N$  is the total number of molecules,  $V$  is the container's volume,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature.

The kinetic theory of gases provides its own expression for the pressure

$$p = \frac{1}{3} \frac{N}{V} m v^2 \quad (5)$$

where  $m$  is the molecular mass and  $v$  is the molecular speed (specifically, the root mean square speed).

We can equate the two expressions for the pressure and then rearrange factors to isolate the kinetic energy

$$\frac{1}{2} m v^2 = \frac{3}{2} kT \quad (6)$$

While a true statement, the equation does not provide us with a meaning for temperature. We may not take the equation to imply that "absolute temperature means the average kinetic energy (within a constant factor)." There are at least two reasons why the equation does not provide an acceptable meaning for temperature.

① Equation (6) is strictly a classical result. When the gas is no longer dilute or the temperature is low, quantum physics becomes essential to a correct description. (Intermolecular forces become significant, too, but that is a separate issue.) When quantum physics just begins to be important, Eq. (6) must be replaced by

$$\frac{1}{2} m v^2 = \frac{3}{2} kT \left[ 1 + C \frac{N}{V} \frac{h^3}{(2\pi m k T)^{3/2}} \right] \quad (7)$$

Here  $h$  denotes Planck's constant, and the constant  $C$  depends on the species of gas.<sup>2,3</sup> For example, for  $^4\text{He}$ , the usual helium isotope with two neutrons, the constant  $C$  is  $-(2^{-3/2})$ ; for  $^3\text{He}$ , the rare isotope with only one neutron, the constant is  $+(2^{-3/2})$ . The average kinetic energy depends on number density  $N/V$  as well as on

temperature, and the dependence on  $T$  is complicated. (Editor's Note: For 1 mole of  $^4\text{He}$ , compressed to 1 liter at 10 K, the correction factor is 0.2 percent.) We would not be tempted to use this more exact equation to ascribe a meaning to temperature based on average kinetic energy. (Moreover, note this: in a mixture of  $^3\text{He}$  and  $^4\text{He}$  gases, with each gas specified to have the same number density  $N/V$  and certainly having the same temperature, the average kinetic energies would differ between the two isotopes because the constants  $C$  differ in sign. At the same temperature, you can have different average kinetic energies—surely temperature cannot mean average kinetic energy.)

② When a kitchen oven is baking brownies, it is filled with radiation, mostly infrared radiation. The energy density of that radiation grows as the fourth power of the absolute temperature

$$\left( \begin{array}{c} \text{energy per unit volume} \\ \text{of radiation} \end{array} \right) = \left( \begin{array}{c} \text{universal} \\ \text{constant} \end{array} \right) T^4 \quad (8)$$

We can solve this equation for  $T$

$$T = \left( \frac{\text{energy density}}{\text{universal constant}} \right)^{1/4} \quad (9)$$

But we would not be tempted to say, "Oh, now I know what temperature means. It is the fourth root of the radiant energy density."

Just as we do not use Eq. (8) or (9) to give a meaning to temperature, so we should not use Eq. (6) to try to give a meaning. All three equations are valid instances in which temperature plays a role in determining physical properties related to energy, but we should not push the equations beyond that.

## Some Thermal Surprises

**Negative absolute temperatures.** Experiments can produce temperatures below absolute zero: negative absolute temperatures. The first such experiment was performed by Edward Purcell and Robert Pound in 1951; their physical system was the assembly of nuclei in a crystal of lithium fluoride.<sup>4,5</sup> (In more detail, the system was the nuclei acting as though they were tiny spinning bar magnets. That aspect of the nuclei was adequately decoupled from the nuclei acting as though they were vibrating masses, having ordinary kinetic energy; the latter aspect cannot exhibit a negative temperature.) By swiftly reversing an external magnetic field and achieving internal magnetic thermal equilibrium before a second reversal occurred, Purcell and Pound produced a final temperature of  $-350 \text{ K}$ .

(A technical aside. One would like some microscopic picture of how the negative temperature was achieved. The interactions of the magnetic moments among themselves are crucial. In a crystal, a magnetic moment interacts not only with an external magnetic field but also with the neighboring magnetic moments. Following convention, we call the energy associated with the latter interaction the *spin-spin energy*. Initially, the spin system is at a

positive temperature, with the nuclear magnetic moments predominantly parallel to the external field, an orientation of negative potential energy. The first field reversal is so fast that the spins cannot respond; they cannot change their orientation during the reversal. Consequently, the spins find themselves pointed predominantly antiparallel to the reversed field, an orientation of positive potential energy. In a short time some of this energy is transferred, by mutual interactions, to spin-spin energy. The energy associated with the mutual interactions becomes relatively large. In fact, that energy becomes larger than what one would predict at any positive temperature.

Since the interaction between the spin system and the lattice vibrations is weak, the spin system holds onto that relatively large amount of energy, even as the crystal is transferred for observation from the small external field to a large magnetic field. There is, in fact, so much spin-spin energy around that the magnetic moments "prefer" to line up antiparallel to the new external field, a position of positive potential energy, rather than line up in the usual parallel position, the position of negative potential energy. There is enough energy around so that a spin can easily line up in what is ordinarily an energetically unfavored orientation. This occurs no matter how the crystal, as a macroscopic object, is rotated during the physical transfer from one magnetic field in the laboratory to the other.

Indeed, the examination of the crystal in the large field was quite directly a test for the amount of energy possessed by the nuclear spin system. Purcell and Pound applied electromagnetic radiation at a frequency chosen so that lithium-7 nuclei could flip from an orientation of low to high potential energy by the absorption of a photon. Instead of absorption, they found—as they had hoped—stimulated emission of radiation at that frequency. The spin system had so much energy that spins predominantly flipped to low potential energy orientations and simultaneously emitted a photon. From the direct observation of stimulated emission of radiation—rather than absorption—one infers both that the total magnetic moment is antiparallel to the external field and that the nuclear spin system is at a negative temperature.)

**Negative  $T$  is hotter than positive  $T$ .** At  $T = -350 \text{ K}$ , Purcell and Pound's system of nuclei was hotter than anything at a positive temperature. That is, it would transfer energy to anything at a positive temperature. The experimental test for a negative temperature relied on that property: the nuclei now emitted energy when probed with radio-frequency waves. At ordinary room temperature, they had absorbed such waves. Indeed, all negative temperatures are hotter than all positive temperatures.<sup>6,7</sup>

You cannot get to zero from either side. As their system cooled down, its temperature went from  $-350 \text{ K}$  to  $-1000 \text{ K}$  to  $-\infty$ , which is physically equivalent to  $+\infty$ , and continued through  $+1000 \text{ K}$  to  $+300 \text{ K}$ , ordinary room temperature. The system did not pass through absolute zero.