

TEMPERATURE FLUCTUATION: AN OXYMORON

Charles Kittel

An oxymoron, according to Webster, is a combination of contradictory words, such as "sweet sadness" or "military intelligence." "Temperature fluctuation" is an oxymoron because the consistent and consensual definition of temperature admits no fluctuation.

For the past century there has been a reliable definition of temperature; we can be very grateful for it without being unnecessarily pedantic about obvious and unambiguous extensions of the usage. Temperature is precisely defined only for a system in thermal equilibrium with a heat bath: The temperature of a system A, however small, is defined as equal to the temperature of a very large heat reservoir B with which the system is in equilibrium and in thermal contact. Thermal contact means that A and B can exchange energy, although insulated from the outer world.

The system A may even be a single atom of a gas. Then the reservoir B is composed of all the other atoms of the gas, along with perhaps the walls of the common container. We do not speak of the single atom as having a fluctuating temperature that tracks its fluctuating kinetic energy.

(J. Lindhard has given a careful discussion of the so-called complementarity relation $\Delta E \Delta T = k_B T^2$ between energy and temperature.¹ He concludes that "the fluctuations . . . are not independent, so that it is not an uncertainty relation, where the fluctuations must be independent." He comments: "Now, there appears to be something quite strange in this result of Rosenfeld. . . . In fact, the canonical ensemble one conceives as having an exact temperature T and a finite energy fluctu-

ation, in disagreement with [the complementarity relation]. Similarly, if we have a system with vanishing ΔE it is hard to imagine that the fluctuation ΔT is unlimited large.")

The inverse of the temperature of the reservoir is given by dS/dU , where S and U are the entropy and temperature of the reservoir. The reservoir must be sufficiently large and complex that the density of states of B is a continuous function of U . Thus a small planetary system, a single atom with its electrons, and a nucleus are excluded as reservoirs. In our logical structure these can be systems, but not reservoirs. Some nuclear physicists, among others, would like to relax the definition of temperature to include small systems as reservoirs, and to imagine temperature fluctuations; but to thus loosen the definition leaves us without a clear, reliable definition of a central concept of physics.

Desperate measures are often urged for the treatment of small systems. Let A be a two-state system such as a proton spin in a magnetic field. The entropy of the isolated system is not well defined, and the derivative dS/dU is meaningless until we define the temperature by bringing A into contact with a large reservoir B. Then the small system has a temperature, a partition function, a free energy, energy fluctuations and an entropy. Now there is no difficulty with the thermodynamics of a small particle—but we must have the reservoir.

Energy fluctuations in a local region of a system also exist, even when the system is in equilibrium. If $u(T)$ is the energy of a local region having volume V , the energy fluctuations are described² by the equation

$$\langle (\Delta u)^2 \rangle = k_B T^2 \left(\frac{\partial u}{\partial T} \right)_{N,V}$$

It would be incorrect, because it

implies too much that is not true, to say that these energy fluctuations can be described as temperature fluctuations. By writing $\Delta u = CV \Delta T$ we can express Δu in terms of a symbol ΔT , where C is the heat capacity per unit volume, but there is no reason to assume that a distribution over states (internal to V), if calculated for $T + \Delta T$, would be the correct distribution. However, it is sometimes a convenient assumption and no doubt will continue to be made. Such an assumption is particularly useful if one needs to invoke a transport equation to obtain the time dependence of a correlation function. As an example, in the problem of light scattering the real physics is determined by the local isothermal fluctuations of the energy and particle number densities, but it is convenient to introduce the thermal conductivity to describe the diffusion of energy density.

In a mature science 90 years after its foundation (by Josiah Willard Gibbs and others), it is inappropriate to overlook or to fiddle with a central and indispensable definition. Even international committees have not done this. Workers who need a less rigorous definition of temperature can always define and label a suitable effective temperature; then what they are doing will not be confused with thermodynamics.

• • •

I am grateful for discussions at various times with Martin J. Klein, Eugenio M. Lifshitz and Herman Feshbach.

References

1. J. Lindhard, "Complementarity Between Energy and Temperature," in *The Lesson of Quantum Theory*, J. de Boer, E. Dal, O. Ulfbeck, eds., North Holland, New York (1986).
2. J. W. Gibbs, *Elementary Principles in Statistical Mechanics*, Yale U. P., New Haven, Conn. (1902), equation 205. ■

Charles Kittel is professor of physics emeritus at the University of California, Berkeley. He has worked mainly in solid-state physics.