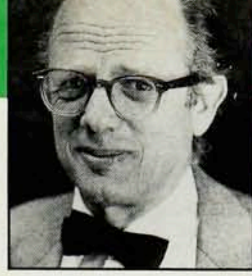


SMALL SYSTEMS: WHEN DOES THERMODYNAMICS APPLY?

Herman Feshbach

The connection between statistical mechanics and thermodynamics is customarily established in the limit of large N, where N is the number of particles in the system under consideration. But how large is "large"? How small can N be without the concepts of temperature and entropy losing their applicability? Fifty years ago Victor Weisskopf, Lev Landau and J. Frenkel introduced the concept of temperature in nuclear reactions, where it has proven to be most valuable. More recently other small systems—single molecules, atomic clusters ranging from two to several hundred atoms, helium droplets and so on—have become interesting objects for study. I shall refer here mostly to the nuclear case, where the question becomes: At a given excitation energy, and assuming equilibrium (not a trivial assumption), how many nucleons must a nucleus contain for the temperature to serve as a quantitative measure of the excitation of the nucleus?

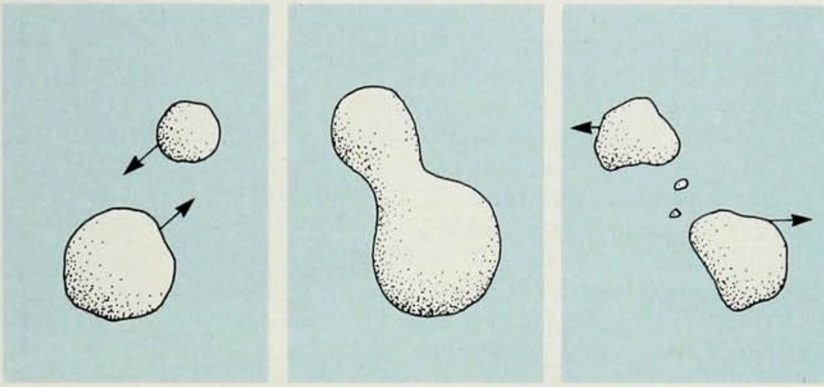
To derive the temperature experimentally, one observes the energy spectrum of a reaction product. The nucleus, which is considered to have been excited to a given temperature in the course of a collision, "evaporates." From the energy distribution of the products one obtains the density of states (the number of states per unit energy) of the residual nucleus, and from that density, the temperature T of the residual nucleus. On examining the statistical mechanical relationship between the density of states and the properties of the system, one discovers that energy and $1/T$ are complementary variables, just like frequency and time. In the latter case we have the familiar result

$$\Delta\omega\Delta t \approx 1$$

where t is the time, ω is 2π times the frequency and $\Delta\omega$ and Δt are the root mean square fluctuations in ω and t. Multiplying this equation by Planck's constant gives the Heisenberg uncertainty relation. In the present case the relationship becomes

$$\Delta E \Delta(1/T) \approx 1 \qquad (1)$$

where E is the energy and T the temperature in energy units. In other words, for the temperature to be well defined a sufficiently large number of states, with a correspondingly large energy spread ΔE, must be populated. If only one state were excited ($\Delta E = 0$), temperature would not be defined.



Collision between nuclei. If each nucleus contains sufficiently many nucleons one can describe the process with the tools of statistical mechanics. For example, one can usefully define a temperature for the products of the collision.

A useful picture is provided by imagining the excited nucleus to be contained in a large "box" with reflecting walls, permitting the establishment of thermal equilibrium. The nucleons outside of the nuclear volume act as a heat reservoir that exchanges energy and mass with the nucleus and thereby induces the fluctuations ΔE and $\Delta(1/T)$. From statistical mechanics one obtains the average square fluctuation

$$(\Delta E)^2 = T^2 \frac{\partial U}{\partial T} = T^2 C_V$$

where U is the excitation energy and C_V is the heat capacity. Substituting this into the uncertainty relation (equation 1) yields

$$\frac{\Delta T}{T} = \left(\frac{\partial U}{\partial T}\right)^{-1/2} = (C_V)^{-1/2}$$

Thus the temperature is well defined when the amount of energy required to change the temperature is large. Since C_V is proportional to the number of particles, N, in the system, $\Delta T/T$ is proportional to $1/\sqrt{N}$. In the macroscopic case N is roughly on the order of 10^{23}, and $\Delta T/T$ is negligible.

In the nuclear case, guided by the model that assumes the nucleus to be a gas of nucleons (the Fermi gas model), U is empirically $(1/\alpha)NT^2$, with α equal to 8 MeV. Using that value in equation 1 yields

$$\frac{\Delta T}{T} = \frac{2}{\sqrt{NT}} = \left(\frac{2\ \text{MeV}}{NU}\right)^{1/4} \qquad (2)$$

Equation 2 imposes a significant constraint on the quantitative use of the temperature concept. For example, if U is 81 MeV, N must be greater than

Herman Feshbach is a nuclear theorist who was chairman of the MIT physics department for ten years.

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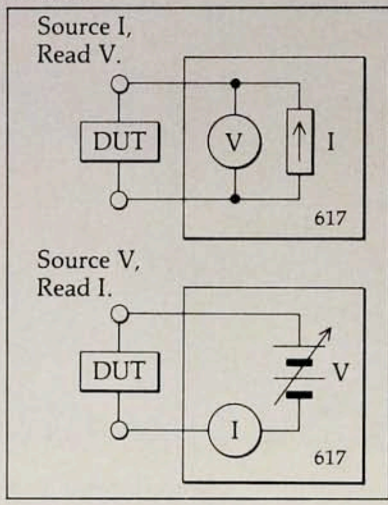

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256 for $\Delta T/T$ to be less than 0.1. If N is 16 (the oxygen nucleus), $\Delta T/T$ is 0.2. Thus the quantitative use of temperature for small systems requires care, although it remains valuable as a qualitative description of the state of excitation.

There is more: Fluctuations become important as one approaches a change in phase, and are especially so at a critical point. This is because the number of states available to the system rises or falls sharply as the phase changes. For the functional form for the density of states not to be modified as a consequence, the condition

$$\frac{T}{C_V}\frac{\partial C_V}{\partial T} \ll \sqrt{C_V} \qquad (3)$$

must hold. This is again a condition on the number of particles in the system. It is easily satisfied, except at the critical point, by macroscopic systems. It can fail when N is relatively small even if the system is at some distance from a phase change.

When $\Delta T/T$ is large or equation 3 is not satisfied, the density of states takes on a new functional form, and one must reconsider the connection between statistical mechanics and thermodynamics.

By using the first law of thermodynamics one can relate the temperature fluctuation to the fluctuation in the entropy S. The relation is

$$\begin{aligned} T\mathrm{d}S &= C_V\mathrm{d}T \\ &= \mathrm{d}U \end{aligned}$$

The entropy is taken to be the log of the density of states, which one estimates again using the Fermi gas model of the nucleus as a guide. In the nuclear case one obtains

$$\begin{aligned} \frac{\Delta S}{S} &= \left(2\frac{\partial U/\partial T}{NU}\right)^{1/2} \\ &= \left(\frac{2\ \mathrm{MeV}}{NU}\right)^{1/4} \end{aligned}$$

where ΔS is the fluctuation in the entropy and we have again used the empirical relationship that U is equal to $NT^2/(8\ \mathrm{MeV})$. The fractional fluctuations in entropy and temperature are accidentally equal in the nuclear case. The consequences described immediately after equation 2 apply equally to the entropy.

These observations, which are based on rather simple considerations, suggest that for small systems thermodynamics is not always quantitatively valid, and therefore requires appropriate modification.

* * *

I am indebted to John Negele for very helpful comments. ■