

TEMPERATURE DEFINED FROM ENTROPY

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The concept of entropy as $k \ln \Omega$, where Ω is the multiplicity of the macrostate in which the system is found, can be used to define the temperature of the system. Here's a summary of the argument.

We'll use two interacting Einstein solids with $N_A = 300$ and $N_B = 200$, with $q = 100$ total energy quanta. The multiplicity function for each solid is

$$\Omega_{A,B} = \binom{q_{A,B} + N_{A,B} - 1}{q_{A,B}} \quad (1)$$

and the total multiplicity of the combined system is

$$\Omega_{total} = \Omega_A \Omega_B \quad (2)$$

The entropies are therefore

$$S_{A,B,total} = k \ln \Omega_{A,B,total} \quad (3)$$

where we pick the subscript for the system we're interested in. We can plot the three entropy curves as functions of q_A (remember $q_B = q - q_A$), to get Fig. 1.

Here the top red curve is S_{total} , the violet curve is S_A and the turquoise curve is S_B . S_{total} reaches a maximum at $q_A = 60$ which is the macrostate where the energy is evenly distributed among all the oscillators. At this point, therefore

$$\frac{\partial S_{total}}{\partial q_A} = 0 \quad (4)$$

Since $S_{total} = S_A + S_B$, this implies that

$$\frac{\partial S_A}{\partial q_A} + \frac{\partial S_B}{\partial q_A} = 0 \quad (5)$$

Since $q_A = q - q_B$, $dq_A = -dq_B$ so we can write this as

$$\frac{\partial S_A}{\partial q_A} = \frac{\partial S_B}{\partial q_B} \quad (6)$$

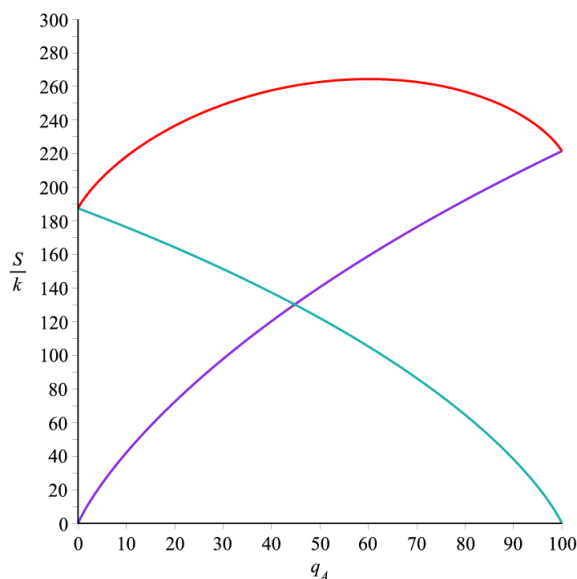


FIGURE 1. Entropy curves.

In the small scale system here, it's not quite right to consider q_A and q_B as continuous variables, so the partial derivatives are an approximation. In very large systems, however, the quanta merge into a continuous energy variable U , so we can write

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \quad (7)$$

As the units of entropy are J K^{-1} and of U are J , this derivative has the dimensions of K^{-1} or the reciprocal of temperature. We can therefore *define* temperature to be

$$\frac{1}{T} \equiv \frac{\partial S}{\partial U} \quad (8)$$

where the partial derivative implies that we hold everything else apart from the energy of the system constant while taking the derivative. Thus two systems that can exchange energy until they reach their most probable macrostate will end up with the same temperature, so they are in thermal equilibrium.

The relation 6 states that the slopes of the entropy-versus-energy curves are equal for the most probable macrostate. In the graph above, this means that the slope of the turquoise line is the negative of the slope of the violet line at $q_A = 60$, which looks about right if you eyeball the graph. We could prove it by taking the actual derivatives, but we'll make do with a numerical example.

Suppose each energy quantum has a value of $\epsilon = 0.1 \text{ eV} = 1.6 \times 10^{-20} \text{ J}$. We can then estimate the temperatures of the two solids at $q_A = 60$ by calculating the slope of the line connecting the points for $q_A = 59$ and $q_A = 61$. For solid B , we use $q_B = 100 - q_A$ so the two energy points are $q_B = 39$ and $q_B = 41$. We get

$$T_A = \frac{61\epsilon - 59\epsilon}{S_A(61) - S_A(59)} \quad (9)$$

$$= \frac{2}{169.92 - 157.35} \frac{\epsilon}{k} \quad (10)$$

$$= 0.56 \frac{1.6 \times 10^{-20}}{1.38 \times 10^{-23}} \quad (11)$$

$$= 659.6 \text{ K} \quad (12)$$

$$T_B = \frac{41\epsilon - 39\epsilon}{S_B(41) - S_B(39)} \quad (13)$$

$$= \frac{2}{107.04 - 103.49} \frac{\epsilon}{k} \quad (14)$$

$$= 0.56 \frac{1.6 \times 10^{-20}}{1.38 \times 10^{-23}} \quad (15)$$

$$= 659.6 \text{ K} \quad (16)$$

Thus the two temperatures are indeed equal at $q_A = 60$.

For $q_A = 1$ we can use the slope between $q_A = 0$ and $q_A = 2$ for solid A and $q_B = 98$ and $q_B = 100$ for solid B . We get

$$T_A = \frac{2\epsilon - 0\epsilon}{S_A(2) - S_A(0)} \quad (17)$$

$$= \frac{2}{10.72 - 0} \frac{\epsilon}{k} \quad (18)$$

$$= 0.187 \frac{1.6 \times 10^{-20}}{1.38 \times 10^{-23}} \quad (19)$$

$$= 216.4 \text{ K} \quad (20)$$

$$T_B = \frac{100\epsilon - 98\epsilon}{S_B(100) - S_B(98)} \quad (21)$$

$$= \frac{2}{187.53 - 185.33} \frac{\epsilon}{k} \quad (22)$$

$$= 0.910 \frac{1.6 \times 10^{-20}}{1.38 \times 10^{-23}} \quad (23)$$

$$= 1055 \text{ K} \quad (24)$$

Here, solid B is much hotter than solid A so if they are interacting, there would be a strong tendency for B to transfer some of its energy to A to bring the solids into thermal equilibrium.

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