

Lecture 9: Entropy and Heat

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9.1 Express Temperature with respect to Entropy

Show that during the quasi-static isothermal expansion, the change of entropy is related to the heat input Q by

$$\Delta S = \frac{Q}{T} \quad \rightarrow \quad T = \frac{Q}{\Delta S} \quad (9.1)$$

It looks like T can be expressed as energy divided by entropy.

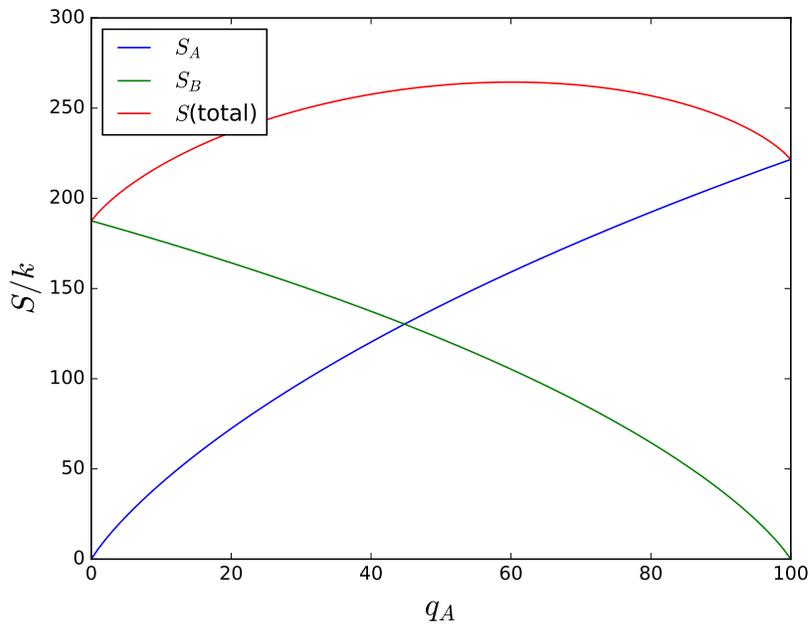


Figure 9.1: Entropy as a function of q_A in two interacting Einstein solids ($N_A=300$, $N_B=200$, $q(\text{total})=100$).

In the context of two interacting Einstein solid, we once calculated Ω as a function of q_A . Let's redo it. At equilibrium, we know S_{total} reaches the maximum, therefore,

$$\frac{\partial S_{\text{total}}}{\partial q_A} = 0 \quad \rightarrow \quad \frac{\partial S_{\text{total}}}{\partial U_A} = 0 \quad (9.2)$$

Since S_{total} is simply the sum of S_A and S_B , we now know

$$\frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0 \quad \rightarrow \quad \frac{\partial S_A}{\partial U_A} = -\frac{\partial S_B}{\partial U_A} \quad (9.3)$$

At equilibrium, which quantity of A and B becomes equivalent?

The consequence of heat flow?

Check the unit! Yes, the slope of S_A is actually the reciprocal of T .

Therefore we have

$$1/T = \left(\frac{\partial S}{\partial U} \right)_{N,V} \rightarrow T = \left(\frac{\partial U}{\partial S} \right)_{N,V} . \quad (9.4)$$

Exercise

Calculate the slope of S - q graph for various points. (assuming $\epsilon=0.1\text{eV}$, 0.024 eV is about 300 K ,)

1. $q=0, \left(\frac{\Delta S_A}{\Delta U_A} \right)^{-1} = \left(\frac{\Delta S_B}{\Delta U_B} \right)^{-1} =$
2. $q=10, \left(\frac{\Delta S_A}{\Delta U_A} \right)^{-1} = \left(\frac{\Delta S_B}{\Delta U_B} \right)^{-1} =$
3. $q=60, \left(\frac{\Delta S_A}{\Delta U_A} \right)^{-1} = \left(\frac{\Delta S_B}{\Delta U_B} \right)^{-1} =$

9.2 Einstein Solid

$$S = Nk[\ln(q/N) + 1] = Nk\ln U - Nk\ln(\epsilon N) + Nk \quad (9.5)$$

$$T = \left(\frac{\partial S}{\partial U} \right)^{-1} = \left(\frac{Nk}{U} \right)^{-1} \quad (9.6)$$

$$U = NkT \quad (9.7)$$

This is exactly the thermal equipartition theorem applied to an Einstein Solid.

9.3 Ideal Gas

$$S = Nk\ln V + 3/2Nk\ln U - Nk\ln(f(N)) \quad (9.8)$$

$$T = \left(\frac{\partial S}{\partial U} \right)^{-1} = \quad (9.9)$$

$$U = 3/2NkT \quad (9.10)$$

9.4 Measuring Entropy

$$dS = \frac{dU}{T} = \frac{Q}{T} \quad (\text{constant volume, } W = 0) \quad (9.11)$$

$$dS = \frac{C_V dT}{T} \quad (\text{constant volume, } W = 0) \quad (9.12)$$

$$\Delta S = S_f - S_i = \int_{T_i}^{T_f} \frac{C_V}{T} dT \quad (9.13)$$

$$\Delta S = \int_A^B \frac{C_V}{T} dT \quad (9.14)$$

What is S when $T=0$, in principle $\Omega=1$, so $S=0$.

However, solid crystals have residual entropy due to the random orientations, so the configuration at 0K is not 1! For instance, each CO molecule has two possible orientations: CO or OC. Assuming they are completely random, what's the residual entropy of 1 mole CO?

$$S(0K) = k \ln(\Omega) = k \ln 2^N = Nk \ln 2 = 5.8 \text{ J/K}$$

$$S(300K) = S(0K) + C_V \int_0^{300} \frac{1}{T} dT = 5.8 + 2.5 \cdot 8.31 \cdot \ln(300) = 5.8 + 118.50 = 124.30 \text{ J/K}$$

This value looks much smaller than the reference value in the appendix (197.67 J/K), because a constant volume assumption is not realistic.

9.5 Macroscopic view

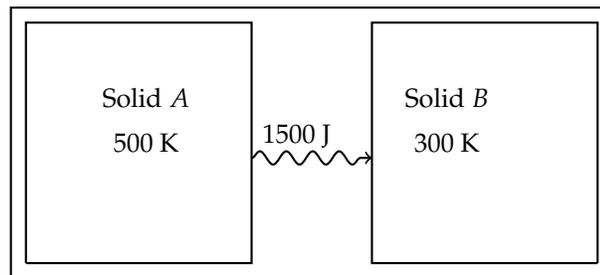


Figure 9.2: A schematic heat flow between two interacting Einstein solids.

1. Object A loses entropy by $dQ/T = -3 \text{ J/K}$
2. Object B gain entropy by $dQ/T = +5 \text{ J/K}$
3. The total entropy increases by $+2 \text{ J/K}$
4. Fundamentally, the net increase in entropy is the driving force behind the flow of heat.
5. The manifestation of 2nd law