

## Today

- I. First take home exam due a week from this Friday
- II. Last Time
- III. An Experimental Example of Going from the Micro- to the Macroscopic
- IV. Entropy and Heat
- V. Thermal and Mechanical Equilibrium

- I. We've been exploring the thermodynamic definition of temperature:

$$\frac{1}{T} \equiv \left( \frac{\partial S}{\partial U} \right)_{V,N} .$$

We applied this to the Einstein solid and to the ideal gas. The results were in perfect agreement with equipartition and illustrated that we'd gotten the constant pre-factor correct.

I. Andrew gave us a guest lecture on two-state paramagnet. By doing the combinatorial calculation of the entropy  $S$ , we were able to find

$$U = -N\mu B \tanh\left(\frac{\mu B}{kT}\right) \quad \text{and} \quad M = N\mu \tanh\left(\frac{\mu B}{kT}\right).$$

The magnetization goes to zero at high temp, at low temp we got a saturated magnetization, as large as it can be, and if we turn off the external magnetic field the magnetization also vanishes.

II. Let's go back to our Einstein solid and ideal gas examples and just take them one more step,

- (i) Einstein solid:  $U = NkT$ ,  $C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = Nk$ .
- (ii) (Monatomic) Ideal gas:  $U = \frac{3}{2}NkT$ ,  $C_V = \frac{3}{2}Nk$ .

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How did we accomplish this? It took roughly 5 steps:

1. Use quantum mechanics and some combinatorics to find an expression for the multiplicity  $\Omega$ , in terms of  $U, V, N$  and any other relevant variables.
2. Take the logarithm to find the entropy  $S$ .
3. Differentiate  $S$  with respect to  $U$  and take the reciprocal to find a relationship between  $T$  and  $U$ .
4. Given the relation of 3., we invert (i.e. algebraically solve if we can) for  $U$  as a function of  $T$  and the other variables.
5. Differentiate  $U(T)$  to get the heat capacity.

### III. How do I experimentally get access to the entropy?

What about trying to probe small changes in the entropy by looking at small changes in the internal energy:

$$dS = \frac{dU}{T} = \frac{Q}{T} \quad (\text{or } dS = \frac{dQ}{T}) \quad (\text{const. volume, i.e. no work})$$

This is Clausius' definition of the entropy. This is directly accessible experimentally.

Generally, the heat transfer will also depend on temperature, and we use a heat capacity to characterize the entropy change

$$dS = \frac{C_V dT}{T},$$

When  $C_V$  is constant we have

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

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In the case of non-constant  $C_V$  we get

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V(T) dT}{T}.$$

As  $T \rightarrow 0$  this integral diverges unless  $C_V(T) \rightarrow 0$  more quickly, then the fact that  $C_V(T) \rightarrow 0$  as  $T \rightarrow 0$  is called the “third law of thermodynamics”.

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When will we have equilibrium? Now the two subsystems can not only exchange energy, but also volume:  $S = S_{\text{total}}$ ,

$$\frac{\partial S}{\partial U_A} = 0 \quad \text{and} \quad \frac{\partial S}{\partial V_A} = 0.$$

Same strategy as before  $S = S_A + S_B$ , so

$$0 = \frac{\partial S}{\partial V_A} = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}.$$

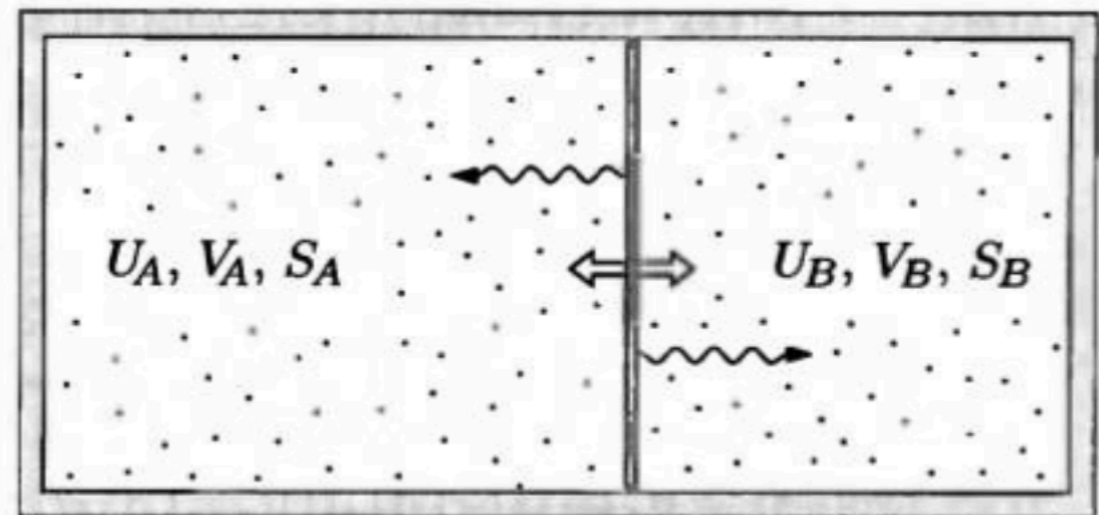
We've shown that

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \quad (\text{at equilibrium}).$$

Investigating the units, we then have

$$T \frac{\partial S_A}{\partial V_A} = T \frac{\partial S_B}{\partial V_B}, \text{ which reasonably leads}$$

$$\text{to } P \equiv T \left( \frac{\partial S}{\partial V} \right)_{U,N}.$$



IV. Define  $P \equiv T \left( \frac{\partial S}{\partial V} \right)_{U,N}$ . Return to the ideal gas:

$\Omega = f(N)V^N U^{3N/2}$ , then we found  $S = Nk \ln V + \frac{3}{2}Nk \ln U + k \ln f$

Then

$$P = T \frac{\partial}{\partial V} (Nk \ln V) = \frac{NkT}{V} \quad (\text{ideal gas law!})$$

