Notes:

Exam: - Friday Oct. 29, 6 PM, **Room 205** MPHY.

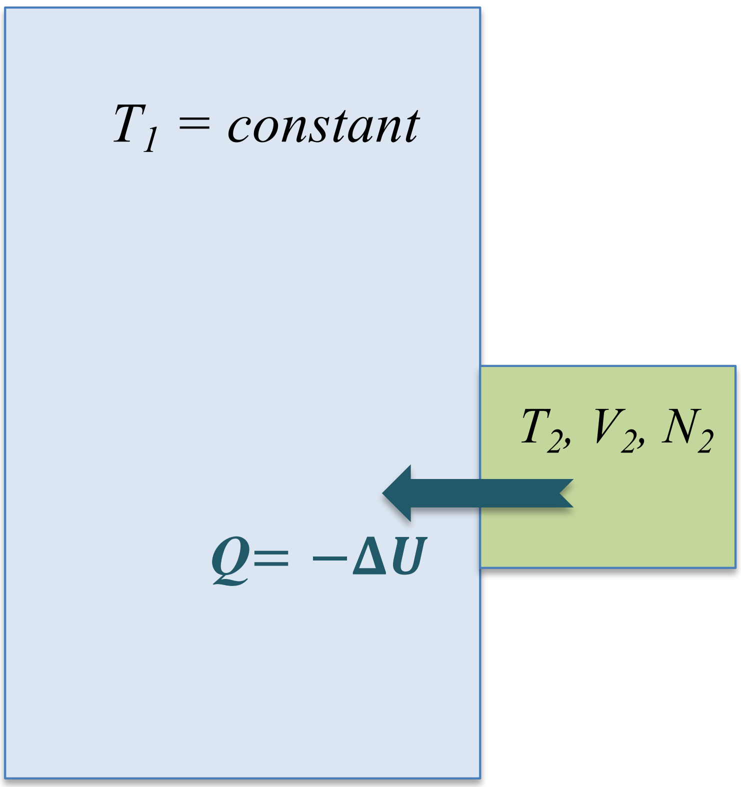
- Coverage through section 6.4. You can make one page formula sheet. 8.5*11 inch, both sides.

Canvas grades & lecture links: sample exams on Canvas now have solutions.

Tomorrow I intend to review; I will accept requests for previous questions from HW etc. to address.

Recall, Canonical Ensemble (ch. 16):

System at constant *T*, in equilibrium with reservoir



At equilibrium, 2 sides can exchange small amounts of energy.

Consider 2 specific microstates in system 2:

$$\frac{P_A}{P_B} = e^{[S_R(A)-S_R(B)]/k_B} = e^{-\Delta E/k_B}$$

Ratio of multiplicities

$$P_i = \frac{1}{Z} e^{-E_i/kT}$$

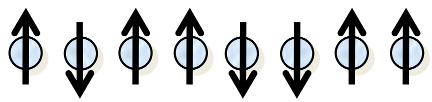
Probability of finding system in state *i* in equilibrium **(one microstate)**

$$Z = \sum_{states\ i} Exp[-E_i/kT]$$

Partition function

Example: spin-1/2 non-interacting paramagnet
(revisit in canonical ensemble):

$E = \pm\mu B$ per atom -> $E = \mu B(N^- - N^+) = \mu B(2N^- - N)$



$$\frac{N^-}{N^+} = e^{-2\mu B/kT}$$

$$Z_i = e^{+\mu B/kT} + e^{-\mu B/kT}$$
$$= 2\cosh \mu B/kT = 2\cosh \beta\mu B$$

- We derived this in thermodynamic limit (I displayed same formula before; microcanonical case).
- For constant-*T* situation this is replaced by *probabilities*.

This is *Z* for system = one atom contacting the rest of the paramagnetic spins at temperature *T*.

Also showed:

$$\beta = \frac{1}{kT}$$

- Energy averaging

$$E_i \rightarrow \langle E \rangle = \text{“}U\text{”} = -\frac{\partial}{\partial \beta} lnZ = kT^2 \frac{\partial}{\partial T} lnZ$$

  - average *E* equivalent to internal energy *U* in thermodynamic limit
  - can show, energy *fluctuations* vanish in thermodynamic limit.

> Works for small *or* large system; contact with infinitely large reservoir maintains the temperature.

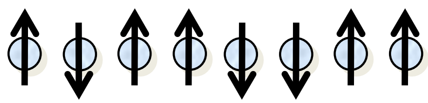
> Results for canonical ensemble approach those for microcanonical in large-*N* limit.

> However internal energy itself is not a conserved quantity.

spin-1/2 non-interacting paramagnet

(revisit in canonical ensemble):

E = $\pm\mu B$ per atom -> $E = \mu B(N^- - N^+) = \mu B(2N^- - N)$



$$\frac{P^-}{P^+} = e^{-{2\mu B}/{kT}}$$

$$Z_i = e^{+{\mu B}/{kT}} + e^{-{\mu B}/{kT}}$$

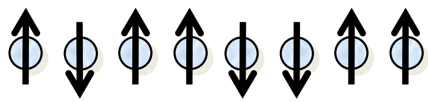
$$= 2\cosh {\mu B}/{kT} = 2\cosh \beta\mu B$$

$Z = \prod_i Z_i$; <u>includes all cross terms</u>.

system of distinguishable particles,
non-interacting.

spin-1/2 non-interacting paramagnet

E = $\pm\mu B$ per atom -> $E = \mu B(N^- - N^+) = \mu B(2N^- - N)$



$$\frac{P^-}{P^+} = e^{-2\mu B/kT}$$

$$Z_i = e^{+\mu B/kT} + e^{-\mu B/kT}$$

$$= 2\cosh \mu B/kT = 2\cosh \beta\mu B$$

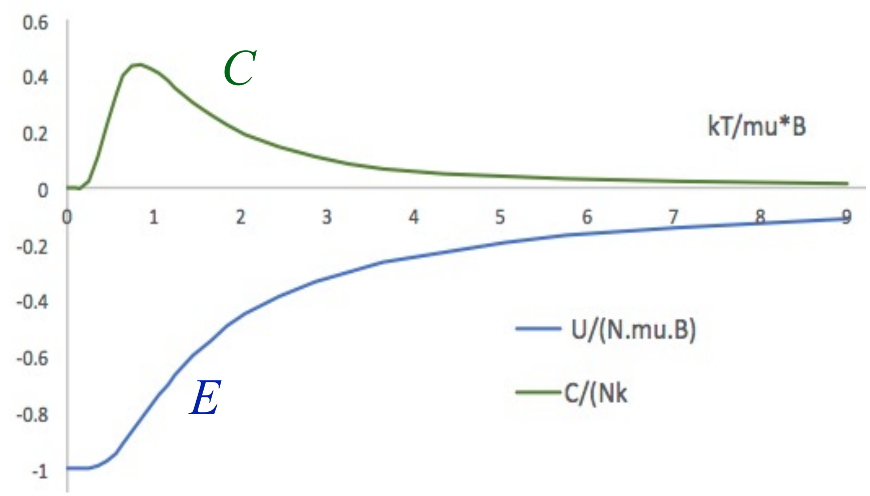
$Z = \prod_i Z_i$; <u>includes all cross terms</u>.

solving:

$$\langle E \rangle = -\mu B N \tanh(\mu B/kT)$$

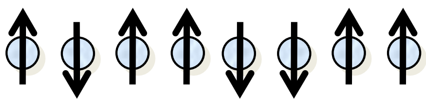
$$C = \frac{\partial \langle E \rangle}{\partial T} = N k_B \frac{(2\mu B/kT)^2}{(e^{\mu B/kT} + e^{-\mu B/kT})^2}$$

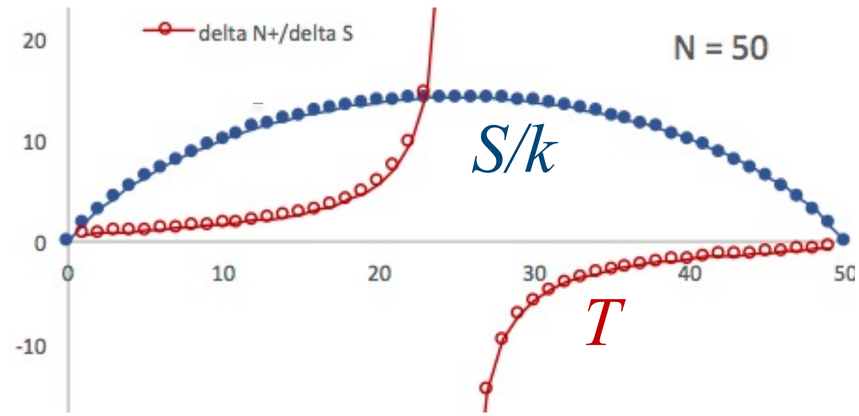
<u>average</u> values for the entire system (not fixed as in microcanonical ensemble).



spin-1/2 non-interacting paramagnet

E = $\pm\mu B$ per atom -> $U = \mu B(N^- - N^+) = \mu B(2N^- - N)$





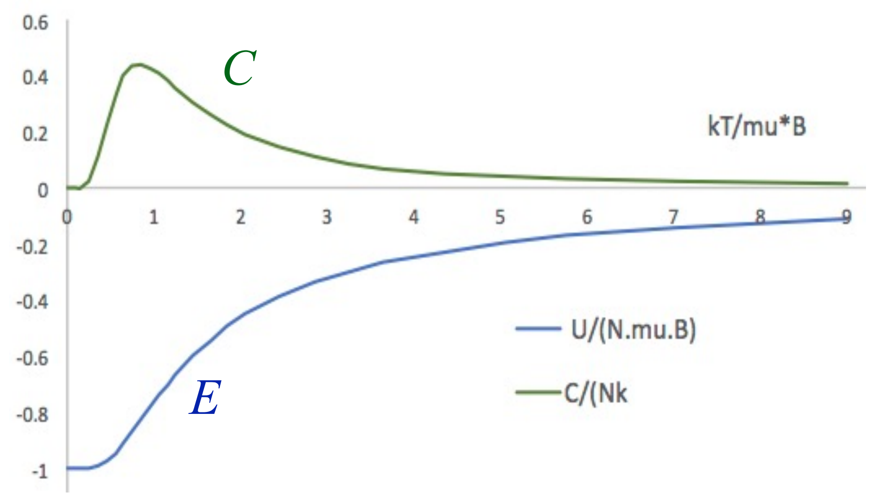
$$S = k_B ln\left(\frac{(N)!}{(N^+)!\,(N^-)!}\right)$$ Microcanonical version

$$\frac{P^-}{P^+} = e^{-{2\mu B}/{kT}}$$ Boltzmann distribution

solving:

$$\langle E \rangle = -\mu BNtanh(\mu B/kT)$$

$$C = \frac{\partial \langle E \rangle}{\partial T} = Nk_B\frac{(2\mu B/kT)^2}{(e^{\mu B/kT} + e^{-\mu B/kT})^2}$$



Canonical ensemble defined quantities:

$$F \equiv -k_B T ln Z$$

- Free energy can treat as defined quantity.
- F is a conserved quantity, doesn't fluctuate.
- Equivalent to thermodynamic F, we will see.

Then other quantities follow as before: $(dF = -SdT - PdV + \mu N)$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

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$$S = k_B lnZ + k_B T \frac{\partial}{\partial T} lnZ$$

$$P = k_B T \frac{\partial}{\partial V} lnZ$$

$$Z = Z(T, V, N)$$

$$\mu = \cdots$$

Canonical ensemble defined quantities:

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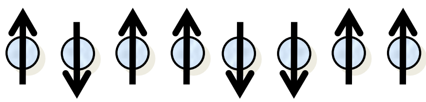
$$S = k_B lnZ + k_B T \frac{\partial}{\partial T} lnZ$$

$$\Longrightarrow \quad F + TS = k_B T^2 \frac{\partial}{\partial T} lnZ = \langle E \rangle$$

spin-1/2 non-interacting paramagnet

E = $\pm\mu B$ per atom -> $E = \mu B(N^- - N^+) = \mu B(2N^- - N)$



$$Z_i = e^{+\mu B/kT} + e^{-\mu B/kT} = 2\cosh\beta\mu B$$

$$\frac{N^-}{N^+} = e^{-2\mu B/kT}$$

$Z = \prod_i Z_i$; <u>includes all cross terms</u>.

solving:

$$\langle E\rangle = -\mu BN tanh(\mu B/kT)$$

$$F = -NkTln(2\cosh\beta\mu B)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

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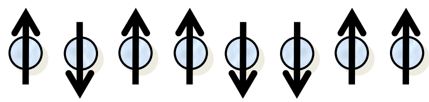

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Plot[Log[2*Cosh[1/x]] - Tanh[1/x]/x, {x, 0, 10}, PlotRange -> All]
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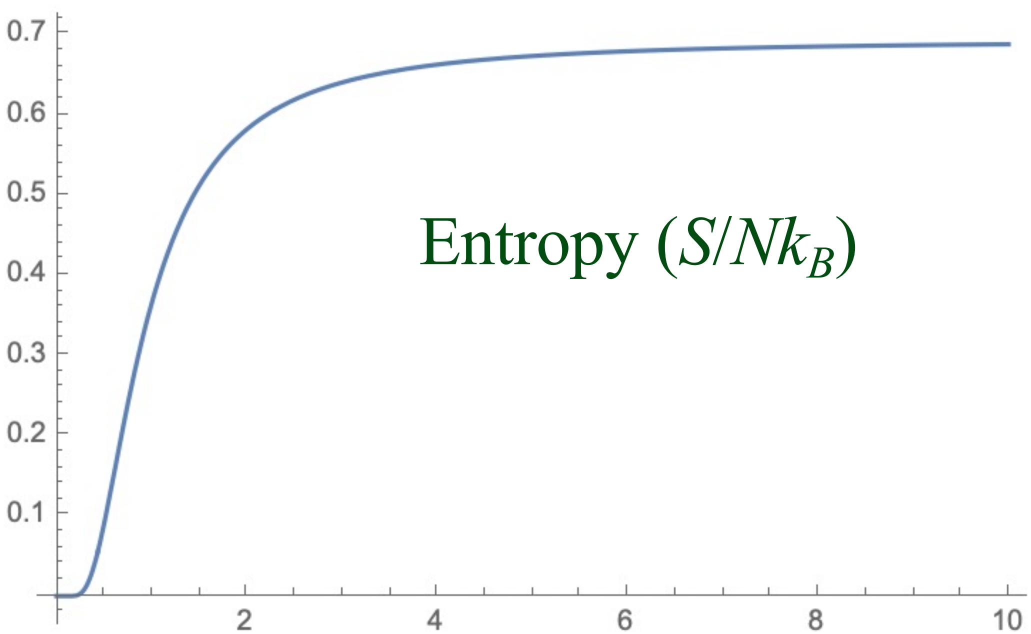
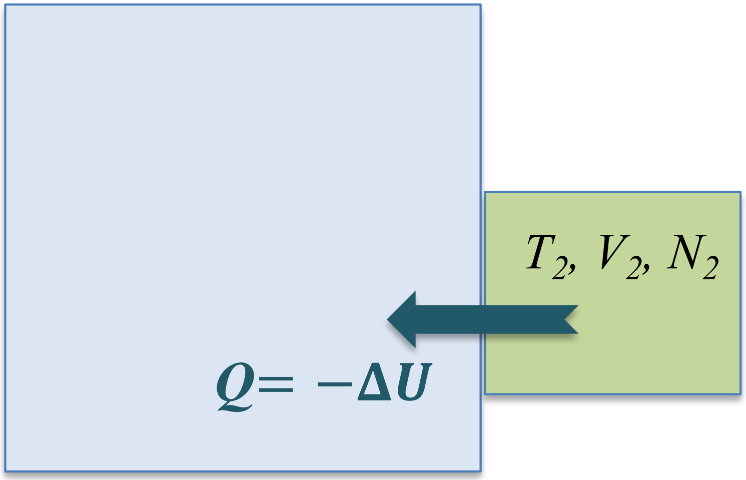


Alternate derivation:



Before, 2 <u>specific microstates</u> in system 2. (microstates have $S = 0$)

$$\frac{P_A}{P_B} = e^{[S_R(A) - S_R(B)]/k_B} = e^{-\Delta E/k_B}$$

<u>Alternative</u>: system 2 in <u>macrostate</u> j with energy E_j (or perhaps $E_j \pm \Delta E$). Probability of j:

$$f_j = \frac{\Omega_{res}(subsystem\ has\ E_j)}{\Omega(all\ possible)} = \frac{exp(\{TS_{res}(U_{sys}) - (E_j - U_{sys})\}/kT)}{exp(\{TS_{res}(U_{sys}) + TS(U_{sys})\}/kT)}$$

True in thermo. limit

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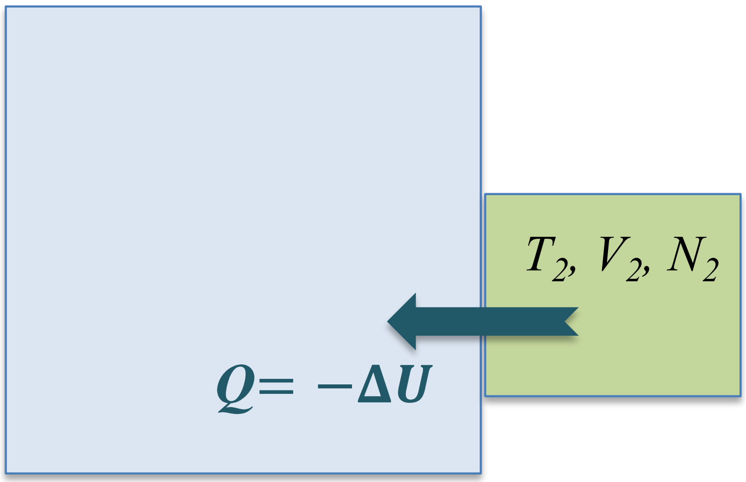

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True in thermo. limit

$$\longrightarrow f_j = e^{\beta F} e^{-\beta E_j}$$

$$F = -k_B T \ln Z \Leftrightarrow Z = e^{-\beta F}$$

Same as our definition, with $F = U - TS$
Probabilities consistent with <u>single-state</u> result.

More on entropy:

$$F \equiv -k_B T lnZ$$

- Free energy can treat as defined quantity.
- F is a conserved quantity, doesn't fluctuate.
- Equivalent to thermodynamic F, we will see.

Then: $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$ $\quad (dF = -SdT - PdV + \mu N)$

$$\Rightarrow \quad S = k_B lnZ + k_B T \frac{\partial}{\partial T} lnZ$$

From here can show:

$$S = -k_B \sum_j P_j \ln(P_j)$$

Gibbs version of entropy, vs. Boltzmann version appropriate for Microcanonical:

$$S = k_B \ln(\Omega)$$