Notes:

Exam:

- Average was 46.
- You can make up some points:
  1. Choose 2 problems. I will post the blank exam.
  2. Work out the solutions from scratch on your own.
  3. Turn in the problems by Thursday in class or Friday afternoon (Tentatively 3 PM, I will arrange to be at my office). Not in my mailbox. Full details to come.
  4. You will get 60% of the made-up points back.
  5. You can look for a few minutes at the exam now but not take it with you.

Homework: Note problem set due Thursday.

Canonical ensemble Recall:

Partition function

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

$$F \equiv -k_B T lnZ$$

$$dF = -SdT - PdV + \mu N$$

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

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

$$\langle E \rangle = k_B T^2 \frac{\partial}{\partial T} lnZ$$

More on entropy:

$$\boxed{F \equiv -k_B T lnZ}$$

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

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

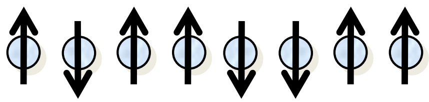
From here can show: $$S = -k_B \sum_j P_j \ln(P_j)$$

Gibbs version of entropy, vs. Boltzmann version appropriate for Microcanonical: $S = k_B \ln(\Omega)$

Note this form of entropy is in chapter 17. Figures prominently in information theory.

spin-1/2 non-interacting paramagnet

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



N distinguishable atoms

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

Also from last time:
Z as *product* of individual components.
Advantageous solution method.

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

(paramagnet specific case)

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

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

Works in general if:

- Energies add (classical *separation of variables*; quantum states as simple product wavefunction);
- Occupation probabilities independent of each other.

Equipartition theorem

- Classical systems (continuum not discrete energies)
- Works in cases having separable variables.
- Requires energy quadratic in position and/or momentum:

$$E = cq^2$$ Text notation (means variables q and p).

Result: for any energy of this general form, easy to show,

$$U = \frac{f}{2} kT$$

from canonical partition function, (1/2)kT obtained for each "degree of freedom" f.

$$Z = \frac{1}{h^{3N}} \iiint d^{3N}r\, d^{3N}p\, e^{-\beta E} \leftarrow Z = \prod_i Z_i;$$ includes all cross terms.

Classical partition function

systems of distinguishable particles, non-interacting.

Equipartition theorem

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Classical partition function

systems of distinguishable particles, non-interacting.

$$Z = \frac{1}{N!}\prod_i Z_i$$

systems of **indistinguishable** particles, still non-interacting case.

Harmonic oscillator systems

- Classical systems:

$$U_i = \frac{\overrightarrow{p_u}^2}{2m} + \frac{\kappa \vec{u}^2}{2} \quad \text{or} \quad U_i = \frac{p^2}{2m} + \frac{\kappa u^2}{2}$$

c.m. coordinates
& reduced mass

Classical partition function

$$Z = \underbrace{\frac{1}{N!\, h^{3N}} \iiint d^{3N}r d^{3N}p e^{-\beta E_{trans}}}_{\langle E \rangle = \frac{3}{2}NkT} \underbrace{\left(\frac{1}{h} \iint dpdue^{-\beta\left(\frac{p^2}{2m}+\frac{\kappa u^2}{2}\right)} \right)^N}$$

$$\langle E \rangle = \frac{3}{2}NkT$$

translational

Internal degrees of freedom
(rotational more important
for e.g. N_2 at room temperature
as we have seen)

Harmonic oscillator systems

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c.m. coordinates
& reduced mass

Classical partition function – harmonic-potential terms only:

$$Z = \left(\frac{1}{h} \iint dp du e^{-\beta\left(\frac{p^2}{2m} + \frac{\kappa u^2}{2}\right)} \right)^N$$

N independent oscillators
(Einstein solid approximation,
ideal gas molecules, etc.)

Equipartition theorem:

- Classical systems (continuum not discrete energies)
- Works in cases having separable variables.
- Requires energy quadratic in position and/or momentum (or other coordinate)
- Vibrations, rotations, translational states. Rotational case in text, won't show here.