Thermodynamics 4230 — Nov. 6, 2011

Lecture Set 6 (Leo Radzihovsky)

Canonical Statistical Mechanics

- Boltzmann weight: system & reservoir
- partition function & Helmholtz free energy
- Examples:
  - paramagnet
  - oscillator
  - Boltzmann ideal gas
- Equipartition
- Maxwell speed distribution

Boltzmann weight

- Recall isolated system:

μ-states: $i = 1, 2, 3, \ldots$

@ fixed E

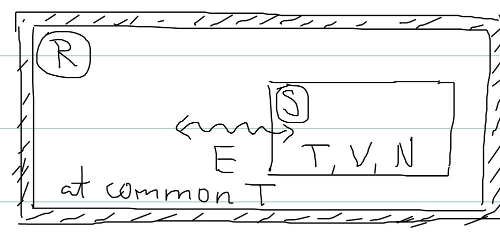
$$\boxed{E, V, N \quad \Omega \rightarrow S = k_B \ln \Omega}$$

probability of state i: $P(i) = \frac{1}{\Omega}$ for all i (same)

$$\sum_i P(i) = 1 = \sum_i \frac{1}{\Omega} = \Omega \cdot \frac{1}{\Omega} \quad \checkmark$$

- system in thermal contact w/ reservoir

$U_{tot} = U_R + E$ fixed $E \ll U_R$



$$P(i) = \frac{1}{Z} e^{-E_i/k_B T}$$

why? use μ-canonical description for R+S

$P(i) \propto$ # μstates in S+R, with S in state i

$$= \Omega_R(U_{tot} - E_i) \underbrace{\Omega(i)}_{1}$$

$$= e^{S_R(U_{tot} - E_i)/k_B}$$

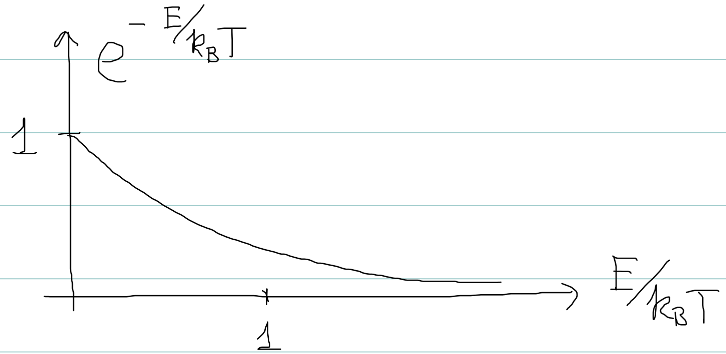
$$P(i) \propto e^{S_R(U_{tot}-E_i)/k_B} = e^{\underbrace{S_R(U_{tot})}_{const} - \underbrace{\left.\frac{\partial S}{\partial U}\right|}_{\frac{1}{T}} E_i} \quad ; \quad E_i \ll U_{tot}$$

$$\Rightarrow P(i) = \frac{1}{Z} e^{-\beta E_i} \quad , \quad \beta \equiv \frac{1}{k_B T}$$

Z ← normalization factor

$$Z = \sum_i e^{-\beta E_i} \rightarrow \underline{\text{the Partition fnc}}$$

(check: $\sum_i P(i) = \frac{1}{Z} \sum_i e^{-\beta E_i} = 1$ ✓)



$$P(i) = \frac{1}{Z} e^{-\beta E_i} \simeq \begin{cases} 1, & \text{for } E_i \ll k_B T \\ 0, & \text{for } E_i \gg k_B T \end{cases}$$

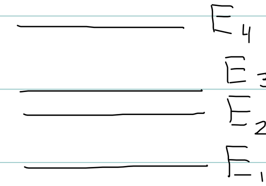
Why?

bigger E_i reduces reservoir's energy $U_{tot} - E_i$

$\Rightarrow$ reduces $S_R \searrow$ with $E_i \nearrow$

Boltzmann distribution

system w/ energy levels E_i



@ temperature T prob. of finding system (e.g. atom) in state i w/ energy $E_i \sim \underline{e^{-\beta E_i}}$

occupation ratio: $\dfrac{n_2}{n_1} = e^{-(E_2 - E_1)/k_B T}$

<u>state i</u> versus <u>energy</u> level E_i

@ each energy level can have many states i

$\Rightarrow$ degeneracy (recall $D>1$ harmonic oscillator: $E^{2d}_{n_x n_y} = \hbar\omega_0 (n_x + n_y)$)

$$P(3,1) = \frac{1}{Z} e^{-\beta \hbar\omega_0 \cdot 4} \quad \leftarrow \text{state } (3,1),\ E_{3,1} = 4\hbar\omega_0$$

$$P(4\hbar\omega_0) = \sum_{n_x n_y}{}' P((n_x, n_y)) = \frac{1}{Z} e^{-\beta 4\hbar\omega_0} \underbrace{\sum{}' 1}_{\underbrace{(4,0),(3,1)\ldots(0,4)}_{5}}$$

$$P(4\hbar\omega_0) = \frac{5}{Z} e^{-\beta 4 \hbar\omega_0}$$

degeneracy factor

$$\Rightarrow P(E_i) = \frac{\Omega(E_i)}{Z} e^{-\beta E_i}$$

degeneracy of $E_i \Leftrightarrow$ multiplicity from μ-canonical distribution

Averages / Statistics

$\langle X_i \rangle = \sum_i X_i P(i)$, where X_i – physical property, $E, V, N, p, \dots$

Ex.'s:

- $U \equiv \langle E_i \rangle = \sum_i \frac{E_i e^{-\beta E_i}}{Z} = -\frac{\partial}{\partial \beta} \ln Z$

$Z(T, \dots)$ gives all of thermodynamics, just like $S(E, \dots)$ for closed system: $\frac{1}{T} = \frac{\partial S}{\partial U} = \beta$

- $-\frac{\partial U}{\partial \beta} = \langle E_i^2 \rangle - \langle E_i \rangle^2 \equiv \sigma_E^2 \Rightarrow \sigma_E = k_B T \sqrt{\frac{C}{k_B}}$

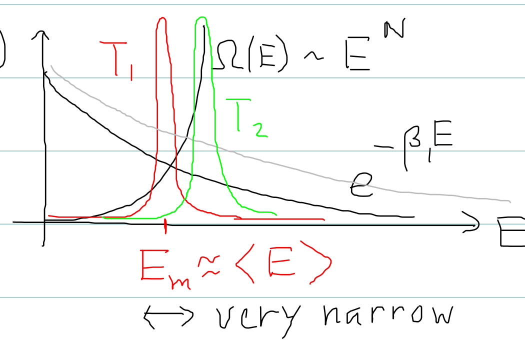
$\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$

energy fluctuations @ fixed T (see 6.16)

- $\langle E_i \rangle = \sum_i \frac{E_i e^{-\beta E_i}}{Z} = \sum_E \frac{E e^{-\beta E}}{Z} \underbrace{\sum_i^{E_i = E} 1}_{\Omega(E)} = \sum_E \frac{E \, \Omega(E) e^{-\beta E}}{Z}$

- $P(E) \propto \Omega(E) e^{-\beta E} / Z$

very fast growing



$P(n)$ vs $\tilde{P}(E)$?

$$\sum_n P(n) = \int dE \underbrace{\left(\sum_n \delta(E - E_n) P(n) \right)}_{\equiv \tilde{P}(E)}$$

Thermodynamics via F

$$\boxed{F = -k_B T \ln Z}$$ compare $S = k_B \ln \Omega$

(on L. Boltzmann grave)

why/how? Helmholtz free energy

$$\frac{\partial F}{\partial T} = -k_B \ln Z - k_B T \frac{\partial}{\partial T} \ln Z = \frac{F}{T} - k_B T \underbrace{\frac{\partial \beta}{\partial T}}_{-\frac{1}{k_B T^2}} \underbrace{\frac{\partial}{\partial \beta} \ln Z}_{-U}$$

$$= \frac{F}{T} - \frac{U}{T} = -S \quad \checkmark$$

(recall: $\underline{dF} = \underline{-S dT} - P dV + \mu dN$)

with:

$$F = -k_B T \ln Z \Rightarrow \text{all of thermodynamics}$$

$$F = U - TS \Rightarrow dF = -S dT - P dV + \mu dN + \ldots$$

equivalently: $Z = e^{-F/k_B T} = \underbrace{e^{S/k_B}}_{\Omega(U)} e^{-U/k_B T}$

$\Omega(U)$ – multiplicity @ energy U

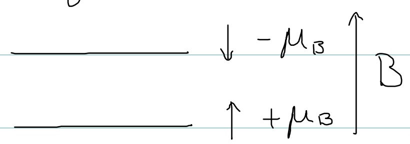
Look @ applications:

- magnet
- harmonic oscillator → solid
- Boltzmann gas
- ⋮

Paramagnet redux

$\boxed{\text{one}}$ magnetic moment μ in B field $\uparrow B$

Ising : two states $\pm\mu_B$ $\quad \underset{\mu}{\uparrow\downarrow}$



$$E_{\uparrow/\downarrow} = \mp \mu_B B$$

$$P(\mu) = \frac{1}{Z} e^{-\left(\frac{-\mu B}{k_B T}\right)} = \frac{1}{Z}\begin{cases} e^{+\frac{\mu_B B}{k_B T}} & , \mu = +\mu_B \ (\uparrow) \\ e^{-\frac{\mu_B B}{k_B T}} & , \mu = -\mu_B \ (\downarrow) \end{cases}$$

- ratio of $\dfrac{P_\downarrow}{P_\uparrow} = e^{-2\mu_B B / k_B T} \ll 1$

- $Z = e^{-\frac{\mu_B B}{k_B T}} + e^{\frac{\mu_B B}{k_B T}} = 2\cosh\left(\frac{\mu_B B}{k_B T}\right)$
- $F = -k_B T \ln Z = -k_B T \ln\left[2\cosh\left(\frac{\mu_B B}{k_B T}\right)\right]$
- $m = \langle \mu \rangle = \dfrac{\sum_\mu \mu e^{+\frac{\mu B}{k_B T}}}{Z} = \mu_B \dfrac{e^{\beta\mu_B B} - e^{-\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} = \mu_B \tanh\left(\frac{\mu_B B}{k_B T}\right) \underset{B\to 0}{\simeq} \left(\frac{\mu_B^2}{k_B T}\right) B$

  $= -\dfrac{\partial}{\partial B} F = +k_B T \dfrac{\partial}{\partial B}\left[\ln\left(2\cosh\left(\frac{\mu_B B}{k_B T}\right)\right)\right]$ ✓
- $U = \langle E \rangle = \langle -\mu B \rangle = -\mu_B B \tanh\left(\frac{\mu_B B}{k_B T}\right) = -\dfrac{\partial}{\partial\beta} \ln Z$ ✓

$\boxed{N}$ moments (independent): $E(\{\mu_i\}) = \sum_i -\mu_i B = -\mu_1 B - \mu_2 B - \ldots$

$$Z_N = \sum_{\{\mu_i\}} e^{\beta \sum_i \mu_i B} = \sum_{\{\mu_i\}} e^{\beta\mu_1 B} e^{\beta\mu_2 B} \ldots e^{\beta\mu_N B} = \left(\sum_{\mu=\pm\mu_B} e^{\beta\mu B}\right)^N$$

$$= (Z_1)^N \Rightarrow M_N = Nm \ , \ E_N = N E_1 \ , \ \text{etc} \ldots$$

Harmonic oscillator

classical:

$$H = \underbrace{\frac{p^2}{2m}}_{\frac{1}{2}k_BT} + \underbrace{\frac{1}{2}m\omega_0^2}_{\frac{1}{2}k_BT} x^2 \quad ?$$

$$E(x,p) = H(x,p)$$

$$Z = \int_{-\infty}^{\infty} \frac{dp\,dx}{2\pi\hbar}\, e^{-\beta\left(\frac{p^2}{2m} + \frac{m\omega_0^2}{2}x^2\right)} = Z_p\, Z_x$$

Gaussian integrals: $I_0(a) = \int_{-\infty}^{\infty} dx\, e^{-\frac{a}{2}x^2} = \sqrt{\frac{2\pi}{a}}$

$$\rightarrow I_2(a) = \int_{-\infty}^{\infty} dx\, x^2 e^{-\frac{a}{2}x^2} = -2\frac{\partial}{\partial a} I_0(a) = \sqrt{\frac{2\pi}{a}}\,\frac{1}{a}$$

$$\rightarrow I_4(a) = \int_{-\infty}^{\infty} dx\, x^4 e^{-\frac{a}{2}x^2} = (-2)^2 \frac{\partial^2}{\partial a^2} I_0(a) = \sqrt{\frac{2\pi}{a}}\,\frac{3}{a^2}$$

} dim. analysis & Γ-fnc's

$\vdots$

$$\rightarrow Z(h,a) = \int_{-\infty}^{\infty} dx\, e^{-\frac{a}{2}x^2 + hx} = \underbrace{\int_{\infty}^{\infty} dx\, e^{-\frac{a}{2}\left(x-\frac{h}{a}\right)^2}}_{\sqrt{\frac{2\pi}{a}}} e^{\frac{h^2}{2a}} = I_0(a)\, e^{h^2/2a}$$

$$= \sum_n \frac{h^n}{n!} I_n(a) \qquad (I_{odd} \text{ vanish})$$

$$Z_p = I_0(\beta/m) \Rightarrow E_p = \frac{-1}{Z}\partial_\beta Z = \frac{-1}{I_0}\partial_\beta \underbrace{I_0(\beta/m)}_{\frac{1}{\sqrt{\beta}}} = \frac{k_BT}{2}$$

$$Z_x = I_0(\beta m\omega_0^2) \Rightarrow E_x = \frac{k_BT}{2}$$

$\Rightarrow$ equipartition: $\underline{U = k_BT}$

<u>Note</u>: $E = E_1 + E_2 + \ldots \Rightarrow Z = Z_1 Z_2 \ldots Z_N$

$$\Rightarrow F = -k_BT \ln Z = -k_BT \ln(Z_1 Z_2 \ldots Z_N) = F_1 + F_2 + \ldots F_N$$

Equipartition Thm

hypotheses:

- quadratic d.o.f.: $E = \frac{1}{2}ax^2 + E_{other}(q)$
- classical d.o.f.: x is a continuous variable

$$U_x = \langle \tfrac{1}{2}ax^2 \rangle = \frac{\int dx \sum_q \left(\frac{1}{2}ax^2\right) e^{-\beta\frac{1}{2}ax^2 - \beta E_{other}}}{Z}$$

$$= \frac{\left(\int dx\ \frac{1}{2}ax^2 e^{-\frac{\beta}{2}ax^2}\right)\left(\cancel{\sum_q e^{-\beta E_{other}}}\right)}{Z_x \qquad \cancel{Z_q}}$$

$$= -\frac{\partial}{\partial\beta}\ln Z_x \underset{\substack{\text{change}\\ \text{vars}}}{=} \frac{k_B T}{2}\,\frac{\int dx\ x^2\ e^{-\frac{1}{2}x^2}}{\int dx\ e^{-\frac{1}{2}x^2}} = \frac{k_B T}{2}$$

classical limit of quantum oscillator:

$$E_n = \hbar\omega_0 n$$

$$Z = \sum_n e^{-\beta\underbrace{\hbar\omega_0 n}_{\varepsilon}} = \frac{1}{\hbar\omega_0}\int_0^\infty d\varepsilon\ e^{-\beta\varepsilon}$$

$$= \frac{k_B T}{\hbar\omega_0}\int_0^\infty d\sigma\ e^{-\sigma}$$

OK for $\frac{\hbar\omega_0}{k_B T} \ll 1$

$$\underline{Z = \frac{k_B T}{\hbar\omega_0}} \Rightarrow Z_N = \left(\frac{k_B T}{\hbar\omega_0}\right)^N \Rightarrow \underline{E = k_B T N}$$

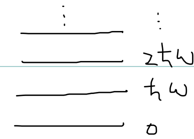
if different ω_0: $\omega_i \Rightarrow Z_N = \prod_{i=1}^{N} \frac{k_B T}{\hbar\omega_i}$

$$\Rightarrow F = -k_B T\sum_i \ln\left(\frac{k_B T}{\hbar\omega_i}\right)$$

Quantum harmonic oscillator

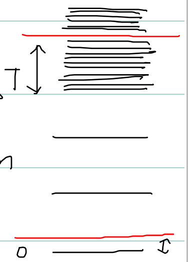
1D: state: n

energy: $E_n = \hbar\omega_0 n$



$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_n e^{-\beta\hbar\omega_0 n} = \sum_n \left(e^{-\beta\hbar\omega_0}\right)^n$$

$$= \frac{1}{1-e^{-\beta\hbar\omega_0}} = \begin{cases} \frac{k_BT}{\hbar\omega_0}, & k_BT \gg \hbar\omega_0, \text{ classical} \\ 1+e^{-\beta\hbar\omega_0}, & k_BT \ll \hbar\omega_0, \text{ quantum} \end{cases}$$



(use $\sum_n x^n = \frac{1}{1-x}$)

$$F = -k_BT \ln Z = k_BT \ln\left(1-e^{-\beta\hbar\omega_0}\right)$$

$\Rightarrow$ all of thermodynamics

e.g. $U = -\frac{\partial}{\partial\beta}\ln Z = +\frac{\partial}{\partial\beta}\ln\left(1-e^{-\beta\hbar\omega_0}\right) = \frac{\hbar\omega_0 e^{-\beta\hbar\omega_0}}{1-e^{-\beta\hbar\omega_0}}$

$$U = \frac{\hbar\omega_0}{e^{\beta\hbar\omega_0}-1} \approx \begin{cases} k_BT, & k_BT \gg \hbar\omega_0, \quad \text{Class.} \\ \hbar\omega_0 e^{-\beta\hbar\omega_0}, & k_BT \ll \hbar\omega_0, \quad \text{Quant.} \end{cases}$$

cf w/ μ-canonical derivation ✓

2D: states: n_x, n_y

energy: $E_{\vec{n}} = \hbar\omega_x n_x + \hbar\omega_y n_y$

$$Z_{2D} = \sum_{n_x n_y = 0}^{\infty} e^{-\beta\hbar\omega_x n_x - \beta\hbar\omega_y n_y} = Z_x Z_y \underset{\text{isotropic}}{=} Z_{1D}^2$$

3D N oscillators: states: $(n_x^i, n_y^i, n_z^i) = \vec{n}^i$

energy: $E_{\vec{n}_i} = \hbar\omega_0 (n_{x_1} + n_{y_1} + n_{z_1} + \ldots 2, 3)$

$$Z_{3D,\text{solid}} = (Z_{1D})^{3N} \Rightarrow F = 3Nk_BT \ln\left(1-e^{-\beta\hbar\omega_0}\right)$$

$$\omega_0 \to \omega_k : \Rightarrow F = 3k_BT \sum_k \ln\left(1-e^{-\beta\hbar\omega_k}\right)$$

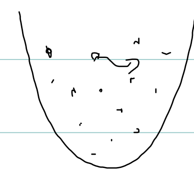
Boltzmann gas

classical:

states: $\vec{p}$

trap potential, e.g. box or $\frac{1}{2} m\omega_0^2 x^2$, ...

energy: $E(\vec{p},\vec{x}) = \frac{p^2}{2m} + V(x)$



$$Z = \frac{1}{N!}\prod_{i=1}^{N}\int \frac{d\vec{p}_i\, d\vec{x}_i}{(2\pi\hbar)^3}\, e^{-\beta\left(\frac{p_i^2}{2m} + V(x_i)\right)}$$

$$= \left(\frac{1}{2\pi\hbar}\, Z_p\, Z_x\right)^{3N} \frac{1}{N!}$$

$$Z_p = \int_{-\infty}^{\infty} dp\, e^{-\beta\frac{p^2}{2m}} = \sqrt{2\pi m k_B T}$$

note:

in classical limit Z_p & Z_x always separate, not quant

$\Rightarrow$ average $O(p)$ & $O(x)$ can be treated independently

ex: $\langle K\rangle = \langle \frac{p^2}{2m}\rangle = \frac{1}{\cancel{Z_x} Z_p}\int dp\, e^{-\beta\frac{p^2}{2m}}\frac{p^2}{2m}\underbrace{\int dx\, e^{-\beta V(x)}}_{\cancel{Z_x}}$

$$\langle K\rangle = \frac{1}{Z_p}\int dp\,\frac{p^2}{2m}\, e^{-\beta p^2/2m} = \frac{k_B T}{2}$$

$$Z_x = \int dx\, e^{-\beta V(x)} \underset{\text{box}}{=} L$$

$$Z = \frac{1}{N!}\left(\sqrt{\frac{2\pi m k_B T}{(2\pi\hbar)^2}}\, L\right)^{3N} = \frac{1}{N}\left(\frac{L}{\lambda_T}\right)^{3N}$$

thermal deBroglie length: $\lambda_T = \sqrt{\frac{2\pi\hbar^2}{m k_B T}} \Leftrightarrow \frac{p_T^2}{2m} \sim \frac{k_B T}{2}$

Maxwell velocity distribution of Boltzmann gas

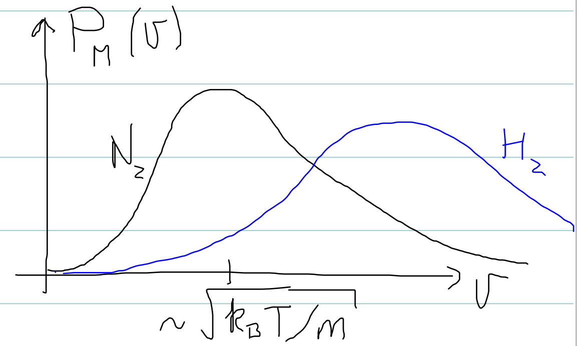
$$P_p(\vec{p}) \propto e^{-\beta \frac{p^2}{2m}} \leftarrow \text{cares about } \vec{p} \text{ (speed + direction)}$$

$\longrightarrow$ change variables $\vec{p} \to v = \frac{p}{m}$ ← speed

$$1 = \int_{-\infty}^{\infty} d^3p \, P_p(\vec{p}) = N \int_0^{\infty} dp \, p^2 4\pi \, e^{-\beta \frac{p^2}{2m}}$$

$$= N \frac{4\pi}{m^3} \int_0^{\infty} dv \, v^2 e^{-\beta \frac{mv^2}{2}} \equiv \int_0^{\infty} dv \, P_{Maxwell}(v)$$

$$\boxed{P_M(v) = \tilde{N} v^2 e^{-\frac{mv^2}{2k_BT}}}$$



energy distribution $E = \frac{1}{2}mv^2$

3D: $\tilde{P}(E) \propto \sqrt{E} \, e^{-E/k_BT}$ ← $\rho(E) \propto E^{\frac{d-2}{2}}$ density of states

$$\int_0^{\infty} \tilde{P}(E) \, dE = \int_{-\infty}^{\infty} d^3p \, P(\vec{p})$$

$$\propto \int \underbrace{dp}_{\frac{dE}{\sqrt{E}}} \underbrace{p^2}_{E} e^{-E/k_BT} \Big\} \, dE \sqrt{E} \quad \checkmark$$