Thermodynamics and Statistics

Degeneracy Pressure

- Suppose you have a rectangular box sides of length L_x, L_y, L_z with the periodic boundary condition
- Non-interacting particle with $H = \dfrac{1}{2m}\left(\vec{p}_x^{\,2} + \vec{p}_y^{\,2} + \vec{p}_z^{\,2}\right)$
- Because of the B.C., $\psi(x, y, z) = \psi(x + L_x, y, z) = \psi(x, y + L_y, z) = \psi(x, y, z + L_z)$, so

$$\psi = \eta \cdot \exp(i(k_x x + k_y y + k_z z))$$

- The number of particles with $E < E_0$ is

$$N(E_0) = d \sum_{n_x, n_y, n_z} \theta\left(E_0 - \frac{1}{2m}\left(\left(\frac{2\pi}{L_x}n_x\right)^2 + \left(\frac{2\pi}{L_y}n_y\right)^2 + \left(\frac{2\pi}{L_z}n_z\right)^2\right)\right)$$

where d is the spin degeneracy. With $\Delta n_x = \dfrac{L_x}{2\pi}\Delta k_x$, we have

$$N(E_0) \approx dL^3 \int \frac{dk_x}{2\pi} \cdot \frac{dk_x}{2\pi} \cdot \frac{dk_x}{2\pi} \cdot \theta\left(E_0 - \frac{|\vec{k}|^2}{2m}\right)$$

$$= dV_0 \int \frac{d^3\vec{k}}{(2\pi)^3} \theta\left(E_0 - \frac{|\vec{k}|^2}{2m}\right)$$

$$= dV_0 \int_0^{k_{max}} \frac{dk}{2\pi^2} k^2 = dV_0 \frac{k_{max}^3}{6\pi^2} \qquad \left[k_{max} = \sqrt{2mE_0}\right]$$

- Fill all energy levels up to E_F
  - $N(E_F) = dV_0 \dfrac{k_F^3}{6\pi^2} = nV_0$, in which $n = \dfrac{k_F^3 d}{6\pi^2}$, so $k_F^2 = \left(\dfrac{6\pi^2 N}{dV_0}\right)^{2/3}$.
  - $\langle E \rangle = dV_0 \displaystyle\int_0^{k_F} \frac{dk}{2\pi^2} k^2 \cdot \frac{k^2}{2m} = \frac{N}{2m} \cdot \frac{\int_0^{k_F} k^4 dk}{\int_0^{k_F} k^2 dk} = \frac{3}{5} N E_F$, in which $E_F = \dfrac{k_F^2}{2m}$.
  - $\langle E \rangle = \dfrac{3}{5} N \cdot \dfrac{1}{2m} \cdot \left(\dfrac{6\pi^2 N}{dV_0}\right)^{2/3}$, so the pressure is

$$P = -\frac{\partial E}{\partial V}\bigg|_N = \frac{2}{5} N \cdot \frac{1}{2m} \cdot \left(\frac{6\pi^2 N}{d}\right)^{2/3} V^{-5/3} = \frac{2}{5}\frac{N}{V} E_F$$

Von Neumann Entropy: $S = -Tr[\hat{\rho} \log \hat{\rho}]$, where $\hat{\rho}$ is density matrix.

- Pure state has $S = 0$.
- If the system is constructed by 2 uncorrelated systems, then $S = S_1 + S_2$.

Find the density matrix so that the entropy maximized with fixed energy.

- With Lagrange multiplier,

$$\delta[\ Tr[\hat{\rho}\log\hat{\rho}] + \beta Tr[\widehat{\rho H}] - \alpha\hat{\rho}\ ] = 0$$

- We got $\hat{\rho}_0 = Z^{-1}e^{-\beta\hat{H}}$, where z is a constant, to preserve $Tr[\hat{\rho}] = 1$, we have $Z = Tr\left[e^{-\beta\hat{H}}\right]$.
- $\beta = \dfrac{1}{k_B T} = \dfrac{1}{T}$ and Z is the partition function.
- $\hat{\rho}_{eq}(\beta) = \dfrac{\exp(-\beta\hat{H})}{Tr[\exp(-\beta\hat{H})]}$ is called canonical thermal distribution or Boltzmann distribution.

With this distribution,

$$\langle E\rangle = \frac{Tr[H\exp(-\beta H)]}{Tr[\exp(-\beta H)]} = -\frac{\partial}{\partial\beta}(\log(Z))$$

$$S_{max} = -Tr[\rho_{eq}\log(\rho_{eq})] = -Tr[\rho_{eq}(-\beta H - \log Z)] = \beta E + \log Z$$

$$\frac{\partial S}{\partial E} = \beta$$

Define $Z = \exp(-\beta F)$, then we have $S = \beta(E - F)$ and $F = E - TS$.
If all N states within $[E, E + \Delta E]$ have the same probability, we have the entropy

$$S = -Tr\left[\frac{1}{N}\log\left(\frac{1}{N}\right)\right] = \log(N)$$

Thermodynamics collection

Most important one is $dU = TdS - PdV$

$$F = U - TS$$
$$H = U + PV$$
$$G = H - TS = U + PV - TS$$
$$\Phi_G = F - \mu N$$

From the partition function

$$U = -\frac{\partial(\log Z)}{\partial\beta}$$
$$F = -T\log Z$$
$$\Phi_G = -T\log Z_G$$
$$U - \mu N = -\frac{\partial(\log Z_G)}{\partial\beta}$$
$$N_i = T\frac{\partial\log Z_i}{\partial\mu}$$

Three kinds of ensembles:

- Micro canonical ensemble: fix $N, V,\ E$

- Canonical ensemble: fix $N,\ V,\ T$
- Grant canonical ensemble: fix $\mu,\ V,\ T$

At thermal limit $N \to \infty,\ V \to \infty,\ \frac{N}{V}$ fixed, three kinds of ensembles can get the same result.

Ideal gas: classical

- No interaction
- Classical means $k \sim \sqrt{mT}$ and $L \gg \lambda \sim \frac{1}{k}$, so $\sqrt{mT} \cdot L \gg 1$.
- Canonical partition function

$$Z = \frac{1}{h^3} \int d^3q d^3p \exp\left(-\beta \frac{p^2}{2m}\right) = \frac{V}{h^3}(2\pi m T)^{3/2}$$

$$Z_N = Z^N = \frac{V^N}{h^{3N}}(2\pi m T)^{3N/2},\ [N\ \textit{distinguishable particles}]$$

$$Z_N = \frac{Z^N}{N!},\ [N\ \textit{indistinguishable particles}]$$

$$\log N! \approx N \log N - N$$

- Inner energy

$$U = -\frac{\partial(\log Z)}{\partial \beta} = \frac{3}{2}NT$$

- Maxwell velocity distribution

$$\rho(v) = 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} v^2 \cdot \exp\left(-\frac{mv^2}{2T}\right)$$

- S-T equation

$$f = -\frac{T}{V}\log Z = nT\left(\log\left(\frac{nh^3}{(2\pi m T)^{3/2}}\right) - 1\right)$$

$$s = \frac{u-f}{T} = n\left(\frac{5}{2} - \log\left(\frac{nh^3}{(2\pi m T)^{3/2}}\right)\right)$$

- Equipartition Theorem
  - For each d.o.f. with only quadratic term of p or q, contributes equal energy

- Gibbs paradox
  - solution: make particles indistinguishable, so $Z_N = \frac{Z^N}{N!}$

Ideal gas: Bose

- No interaction, assume μ is general for all modes
- Grant partition function

$$Z_i = Tr_i[\exp(-\beta(H_i - \mu N_i))] = \sum_{N_i} \exp(-\beta(\epsilon_i - \mu)N_i) = \frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}}$$

$$Z_G = \exp\left(\sum_i \log(Z_i)\right)$$

- Particle number

$$\langle N_i \rangle = \sum_i N_i \rho_i = \frac{\sum_i N_i \exp(-\beta(\epsilon_i - \mu)N_i)}{1 - \exp(-\beta(\epsilon_i - \mu))} = \frac{1}{\beta}\frac{\partial \log Z_i}{\partial \mu} = \frac{1}{\exp(\beta(\epsilon_i - \mu)) - 1}$$

$$n = \frac{\langle N \rangle}{V} = \int \frac{dk}{2\pi^2} k^2 \cdot \frac{1}{\exp\left(\beta\left(\frac{k^2}{2m} - \mu\right)\right) - 1}$$

$$\langle N_i \rangle = \frac{1}{\beta}\frac{\partial \log Z_i}{\partial \mu} = \frac{1}{\exp(\beta(\epsilon_i - \mu)) - 1}$$

with the expression of $\langle N_i \rangle \geqslant 0$ when $\epsilon_i = 0$, we have $\mu < 0$ for all Bose gas.

- B-E condensate
  - Fixed T: $n_{critical} = n_{max}$
  - Fixed n: $T_{critical} = \frac{2\pi}{m} \cdot \left(\frac{n}{\zeta\left(\frac{3}{2}\right)}\right)^{2/3}$

$$n_{max} = \int \frac{dk}{2\pi^2} k^2 \cdot \frac{1}{\exp\left(\frac{k^2}{2mT}\right) - 1} = \left(\frac{mT}{2\pi}\right)^{3/2} \cdot \zeta\left(\frac{3}{2}\right), \; except\ for\ g.s.$$

- Classical limit
  - $T \to +\infty$ and $\beta\mu \to -\infty$
  - $\langle N_i \rangle \approx \exp(-\beta(\epsilon_i - \mu)) \ll 1$
  - $n \approx \int \frac{dk}{2\pi^2} k^2 \cdot \exp(-\beta(\epsilon_i - \mu)) = \exp(\beta\mu) \cdot 2\left(\frac{mT}{2\pi}\right)^{3/2}$
  - $u \approx \int \frac{dk}{2\pi^2} k^2 \cdot \frac{k^2}{2m} \cdot \exp(-\beta(\epsilon_i - \mu)) = -\frac{\partial n}{\partial \beta} + \mu n = \frac{3}{2} nT$

Ideal gas: photon

- No chemical potential, $\mu = 0$
- 2 polarization directions
- Dispersion relation, $\epsilon = |k|$
- For one mode

$$Z_i = \sum_{N_i} \exp(-\beta\epsilon_i N_i) = \frac{1}{1-\exp(-\beta\epsilon_i)}$$

$$\langle N_i \rangle = \frac{1}{\exp(\beta|k_i|)-1}$$

- Inner energy

$$u(T) = \frac{U}{V} = 2\int \frac{dk}{2\pi^2}k^2 \cdot \frac{k}{\exp(\beta k)-1} = \frac{\pi^2}{15}T^4$$

$$u(\omega,T) = \frac{\omega^3}{\pi^2(\exp(\beta\omega)-1)}$$

- Classical limit: $T \to \infty$ corresponding to ω

$$u(\omega,T) \approx \frac{\omega^3}{\pi^2\beta\omega} = \frac{\omega^2}{\pi^2\beta}$$

$$u(T) = \int_0^\infty d\omega\; u(\omega,T) = \infty$$

but here ω is the integral variable and T is fixed, so the classical limit is not satisfied when $\omega \to \infty$.

Phonons

- Each of modes(ω_i) is basically a harmonic oscillator
- For one mode

$$Z_i = \sum_n \exp\left(-\beta\omega_i\left(n+\frac{1}{2}\right)\right) = \exp\left(-\frac{\beta\omega_i}{2}\right)\frac{1}{1-\exp(-\beta\omega_i)}$$

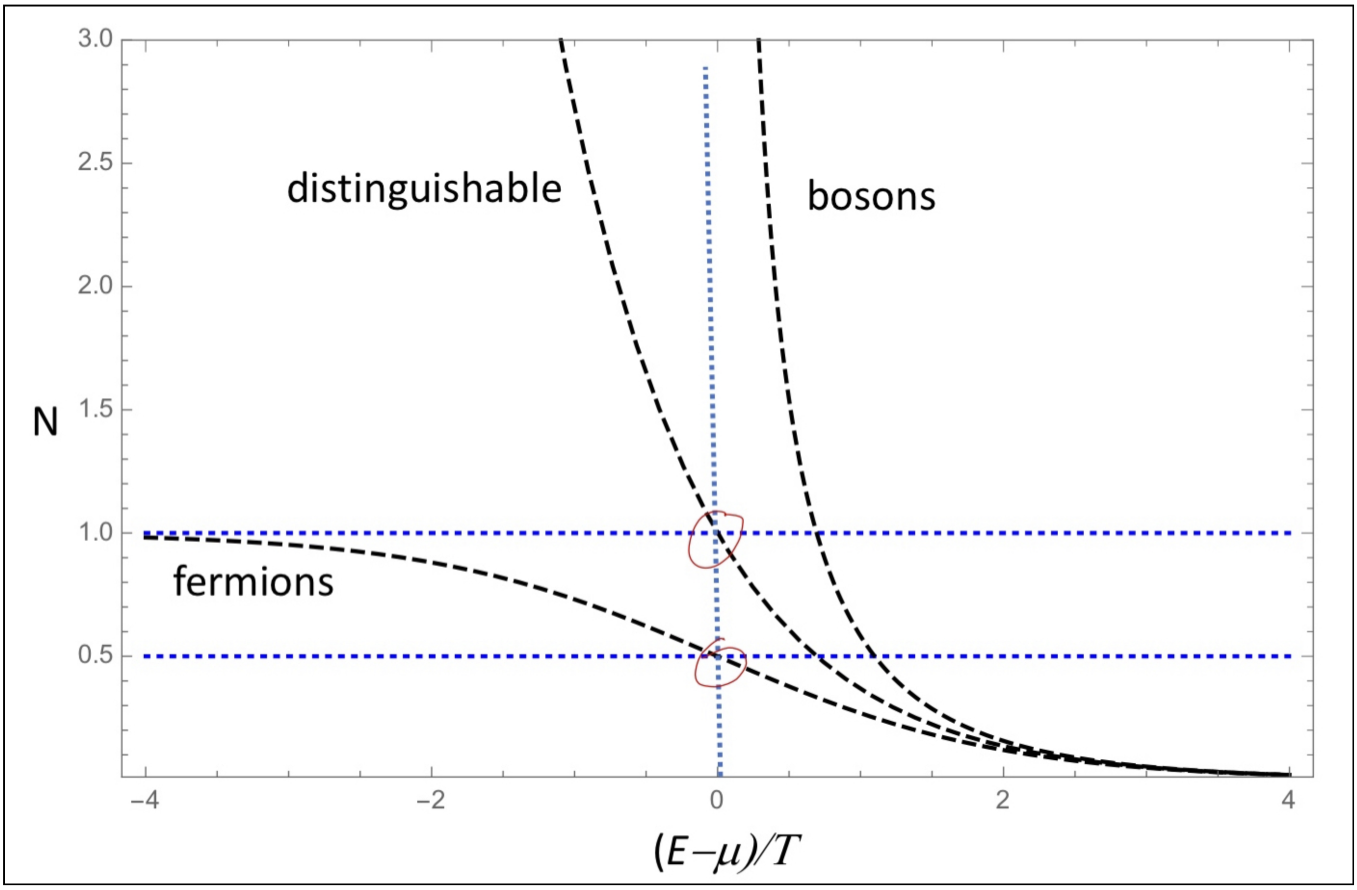
$$\langle E_i \rangle = \frac{-\partial \log Z_i}{\partial\beta} = \frac{\omega_i}{2} + \frac{\omega_i}{\exp(\beta\omega_i)-1};\;\; u(\omega,T) = \frac{\omega^3}{2|v_s|^2\pi^2(\exp(\beta\omega_i)-1)}$$

Ideal gas: Fermi

- For one mode (include spin)

$$Z_i = Tr_i[\exp(-\beta(H_i-\mu N_i))] = 1+\exp(-\beta(\epsilon_i-\mu))$$

$$\langle N_i \rangle = \frac{1}{\beta}\frac{\partial \log Z_i}{\partial\mu} = \frac{1}{\exp(\beta(\epsilon_i-\mu))+1}$$



3.0
2.5
2.0
1.5
1.0
0.5
N
distinguishable
bosons
fermions
−4
−2
0
2
4
$(E-\mu)/T$