Statistical Mechanics Tong Notes

1.1. Introduction - emergent phenomena exist

1.2. Microcanonical ensemble - every state (microstate = same energy) is equally probable → $P(E) = \frac{1}{\Omega(E)}$

$$\frac{1}{T} = \frac{\partial S}{\partial E} \qquad C = \frac{\partial E}{\partial T} \qquad S(E) = k_B \ln \Omega(E)$$

$k_B = 1.381 \times 10^{-23}\, J/K$

$$\Delta S = \int_{T_1}^{T_2} \frac{C(T)}{T}\, dT \quad \text{from} \quad \frac{\partial S}{\partial T} = \frac{\partial S}{\partial E}\frac{\partial E}{\partial T} = \frac{C(T)}{T}$$

$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\left(\frac{1}{T}\right) = \frac{\partial T}{\partial E}\frac{\partial}{\partial T}\left(\frac{1}{T}\right) = \frac{1}{C} \cdot \frac{-1}{T^2} \checkmark$$

Stirling formula: $\ln(N!) = N \ln N - N$

Solving $\frac{1}{T} = \frac{\partial S}{\partial E}$ for E & doing $\partial E/\partial T$ solves $C(T)$ generically.

$\rightarrow P = T\frac{\partial S}{\partial V}$ or $P = \frac{\partial E}{\partial V}$ or $\frac{P}{T} = \frac{\partial S}{\partial V}$ (treat S + Ω as fns of V)

first law: from $dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV \rightarrow dE = TdS - pdV \; (+\mu dN)$

$$C_V = T \left.\frac{dS}{dT}\right|_V = \left.\frac{dE}{dT}\right|_V \qquad C_p = T\left.\frac{dS}{dT}\right|_p \Rightarrow \text{enthalpy dependent}$$

- All microcanonical Ensemble information assumes fixed energies

$$\left[\sum_n^N \lambda^n = \frac{1-\lambda^{N+1}}{1-\lambda}\right] \rightarrow \frac{1}{1-\lambda} \text{ for } N \rightarrow \infty$$

2.3 Canonical Ensemble - allow the energy to vary (against heat reservoir)

System S in contact with fixed T reservoir R has access to all energy states, and all microstates are equally accessible

$\therefore \quad p(n \text{ state}) = \dfrac{e^{-E_n/k_bT}}{\sum_m e^{-E_m/k_bT}} = \dfrac{\Omega(n)}{\Omega(\text{total})} \Rightarrow \Omega(\text{total}) = e^{S_R(\text{total } E)/k_b} \cdot \sum_n e^{-E_n/k_b T}$

$\beta = \frac{1}{k_b T}$

m & n refer to S states & Ω's refer to S+R system (sum over available R spots).

Boltzmann Distribution / canonical ensemble

$$Z = \sum_n e^{-\beta E_n} \qquad \langle E \rangle = \sum_n E_n \, p(n) = \sum_n E_n \frac{e^{-\beta E_n}}{Z}$$

$$= -\frac{\partial}{\partial\beta} \ln(Z) \qquad \& \quad \langle E^2 \rangle = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$$

$$\Delta E^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 \qquad C_v = \left.\frac{\partial \langle E \rangle}{\partial T}\right|_v \qquad \langle \Delta E^2 \rangle = \frac{\partial^2}{\partial \beta^2} \ln(Z) = -\frac{\partial \langle E \rangle}{\partial \beta}$$

$$= k_b T^2 C_v$$

$\frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}} \rightarrow$ as $N \to \infty$ Canonical $\to$ Microcanonical

---

entropy: $\Omega_{micro} = \dfrac{W!}{\prod_n (p(n) W)!}$ for W copies of our canonical ensemble in a big microcanonical ensemble.

$$S_{micro} = k_b \ln(\Omega_{micro}) = -k_B W \sum_n p(n) \ln(p(n))$$

$$\therefore S_{canonical} = -k_B \sum_n p(n) \ln(p(n))$$

With $P(n)$ = Boltzmann Distribution $= e^{-\beta E_n}/Z$

$$S_{canonical} = -\frac{k_B}{Z} \sum_n e^{-\beta E_n} \ln\left(\frac{e^{-\beta E_n}}{Z}\right) = \frac{k_B \beta}{Z} \sum_n E_n e^{-\beta E_n} + k_B \ln Z$$

$$= k_B \frac{\partial}{\partial T} (T \ln Z) = -\frac{\partial}{\partial T}(F)$$

$$S = \frac{\langle E \rangle - F}{T}$$

Free energy $\quad F = \langle E \rangle - TS \quad$ (Helmholtz)

$$dF = d\langle E\rangle - d(TS) = \boxed{-SdT - pdV = dF}$$

from $\boxed{dE = TdS - pdV}$ ($+\mu dN$ to both)

= Legendre transform of E.

$$S = -\frac{\partial F}{\partial T}\bigg|_V, \quad p = -\frac{\partial F}{\partial V}\bigg|_T$$

$$p = -\frac{dF}{dV}$$

$$F = -k_B T \ln(Z)$$

$$dS = \frac{dE}{T} + \frac{pdV}{T}$$

1.4 Chemical Potential + Grand Canonical Ensemble

$$\mu = \frac{\partial E}{\partial N}\bigg|_{S,V} = \frac{\partial F}{\partial N}\bigg|_{T,V} = -T\frac{\partial S}{\partial N}$$

$$\left(\therefore S = k_B \beta^2 \frac{\partial F}{\partial \beta}\right)$$

Grand Canonical Ensemble $\quad E_n \to E_n - \mu N_n \quad$ for all eqns

$$Z(T,\mu,V) = \sum_n e^{-\beta(E_n - \mu N_n)}, \quad P(n) = \frac{e^{-\beta(E_n - \mu N_n)}}{Z}$$

$$S = k_B \frac{\partial}{\partial T}(T\ln(Z)) = -\frac{\partial}{\partial T}(F)\bigg|_{N,\mu}, \quad \langle E\rangle - \mu\langle N\rangle = -\frac{\partial}{\partial\beta}\ln(Z)$$

$$\langle N \rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln(Z), \quad \Delta N^2 = \frac{1}{\beta^2}\frac{\partial^2}{\partial\mu^2}\ln Z = \frac{1}{\beta}\frac{\partial}{\partial\mu}\langle N\rangle$$

Grand Canonical Potential $\quad \Phi = F - \mu N = -pV$

$$d\Phi = -SdT - pdV - Nd\mu$$

(Legendre transform of $F(N) \to \Phi(\mu)$)

$$\Phi = -k_B T \ln(Z)$$

$$dG = -SdT + VdP + \mu dN$$

gibbs free energy

2. Classical Gases

Classical Partition function $\quad Z_1 = \frac{1}{h^3}\int d^3p\, d^3q\, e^{-\beta H(p,q)} \quad H(p,q) = \frac{\vec{p}^2}{2m} + V(\vec{q})$

2.2. Ideal Gas $\quad H = \vec{p}^2/2m \rightarrow Z_1(V,T) = \frac{1}{(2\pi\hbar)^3}\int d^3q\, d^3p\, e^{-\beta \vec{p}^2/2m} = V\left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2}$

$$\int d^3q = V \qquad \int dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

$$Z_1 = \frac{V}{\lambda^3}$$

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}} = \text{thermal de Broglie wavelength}$$

$$P = -\frac{\partial F}{\partial V} = \frac{\partial}{\partial V}(k_B T \ln Z) = \frac{N k_B T}{V} \rightarrow \boxed{PV = NkT}$$

$$\& \quad E = -\frac{\partial}{\partial\beta}\ln(Z) = \frac{3}{2}N k_B T$$

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V = \frac{3}{2}N k_B$$

Gibbs paradox $\quad Z = \frac{V^N}{\lambda^{3N}} \rightarrow \frac{V^N}{N!\,\lambda^{3N}}$

indistinguishable particles

$$S = \frac{\partial}{\partial T}(k_B T \ln(Z)) \underbrace{\approx}_{\text{stirling approximation after } \partial/\partial T} N k_B\left[\ln\left(\frac{V}{N\lambda^3}\right) + \frac{5}{2}\right] \quad \text{Sakur-tetrode eqn}$$

Grand Canonical ensemble $\rightarrow \mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta\mu N}\cdot\left(\frac{V^N}{N!\,\lambda^{3N}}\right) = e^{\frac{e^{\beta\mu}V}{\lambda^3}}$

$$\therefore N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln(\mathcal{Z}) = \frac{e^{\beta\mu}V}{\lambda^3}$$

$$\mu = k_B T \ln\left(\frac{\lambda^3 N}{V}\right) \qquad \rightarrow \Delta N^2 = \frac{1}{\beta^2}\frac{\partial^2}{\partial\mu^2}\ln(\mathcal{Z}) = N$$

$$\& \quad PV = k_B T \ln(\mathcal{Z}) = k_B T\,\frac{e^{\beta\mu}V}{\lambda^3} = k_B T N \Rightarrow PV = NkT \checkmark$$

2.3 Maxwell-Boltzmann Distribution $\qquad p = mv$

$$\therefore Z_1 = \frac{m^3 V}{(2\pi\hbar)^3}\int d^3v\, e^{-\beta m v^2/2} = \frac{4\pi m^3 V}{(2\pi\hbar)^3}\underbrace{\int dv\, v^2 e^{-\beta m v^2/2}}$$

probability distribution $\rightarrow f(v)\,dv = \bar{N} v^2 e^{-mv^2/2k_BT}\,dv$

$$\int_0^\infty f(v)\,dv = 1 \rightarrow \bar{N} = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}$$

$$\langle v^2\rangle = \int_0^\infty dv\, v^2 f(v) = \frac{3k_BT}{m} \rightarrow E = \frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_BT$$

2.4. Diatomic Gas $\rightarrow$ doing Z with rotational KE or SHO hamiltonians yields equipartition expected results.

2.5 Interacting Gases - Cluster expansion (diagrams)

$$\mathcal{Z}(\mu, V, T) = \sum_N e^{\beta\mu N} Z(N, V, T)$$

$$Z(N,V,T) = \frac{1}{\lambda^{3N}}\sum_{\{m_\ell\}}\prod_\ell \frac{U_\ell^{m_\ell}}{(\ell!)^{m_\ell} m_\ell!} \qquad U_\ell = \int\prod_{i=1}^{\ell} d^3r_i \sum_{G\in\{\ell\text{-cluster}\}} G$$

graphs ℓ

$$\therefore \mathcal{Z} = \sum_{m_\ell=0}^{\infty}\prod_{\ell=1}^{\infty}\left(\frac{z}{\lambda^3}\right)^{m_\ell\cdot\ell}\frac{1}{m_\ell}\left(\frac{U_\ell}{\ell!}\right)^{m_\ell} \qquad \underline{z = e^{\beta\mu}} \text{ fugacity}$$

$$\mathcal{Z} = \prod_{\ell=1}^{\infty}\exp\left(\frac{U_\ell z^\ell}{\lambda^{3\ell}\ell!}\right) \quad + \quad \boxed{b_\ell \equiv \frac{\lambda^3 U_\ell}{V\ell!\lambda^{3\ell}}} \qquad U_1 = V \quad \therefore b_1 = 1$$

$$\mathcal{Z} = \prod_{\ell=1}^{\infty}\exp\left(\frac{V}{\lambda^3}b_\ell z^\ell\right) = \exp\left(\frac{V}{\lambda^3}\sum_{\ell=1}^{\infty} b_\ell z^\ell\right)$$

$$\therefore \frac{pV}{k_BT} = \ln \mathcal{Z} = \frac{V}{\lambda^3}\sum_{\ell=1}^{\infty} b_\ell z^\ell$$

$$\& \quad \frac{N}{V} = \frac{z}{V}\frac{\partial}{\partial z}\ln(\mathcal{Z}) = \frac{1}{\lambda^3}\sum_{\ell=1}^{\infty}\ell b_\ell z^\ell$$

$$\text{s.t.} \quad \frac{pV}{Nk_BT} = \frac{\sum_\ell b_\ell z^\ell}{\sum \ell b_\ell z^\ell}$$

3. Quantum Gases

3.1 density of states $g(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$ for free gas in a box

$= \frac{VE}{2\pi^2\hbar^3c^3}\sqrt{E^2-m^2c^4}$ for relativistic particles.

3.2 Blackbody Radiation

$E = \hbar\omega = \hbar k c$ + DOS factor of 2 from polarizations

photons aren't conserved, so $\mu = 0$.

Planck blackbody distribution: $E(\omega)\,d\omega = \frac{V\hbar}{\pi^2c^3}\frac{\omega^3\,d\omega}{e^{\beta\hbar\omega}-1}$

$$\log Z = \frac{-V}{\pi^2c^3}\int_0^\infty d\omega\, \omega^2 \ln\left(1-e^{-\beta\hbar\omega}\right)$$

$$E = -\frac{\partial}{\partial\beta}\ln Z = \frac{V(k_BT)^4}{\pi^2c^3\hbar^3}\int_0^\infty \frac{dx\, x^3}{e^x-1} = \frac{\pi^2 V k_B^4}{15\hbar^3c^3}T^4$$

Stefan Boltzmann law Power flux $= \frac{E}{V}\cdot\frac{c}{4} = \sigma T^4$

$$\sigma = \frac{\pi^2 k_B^4}{60\hbar^3c^2}$$

3.3 Phonons $c \to c_{sound}$, 2 polarizations $\to 3$, max frequency = debye frequency

3.4. Quantum equipartition theorem

3.5 Bosons - when debroglie wave length gets to the same size as space between atoms then spin statistics matters.

$$\langle n_r \rangle = \frac{1}{e^{\beta(E_r-\mu)}-1} = \text{bose-einstein distribution}$$

$z = e^{\beta\mu}$ fugacity $0 < z < 1$ since $\mu < 0$

3.5.3.2 ideal bose gas - its a mess

3.6. Fermions - $n_r = \frac{1}{e^{\beta(E_r-\mu)}+1}$ fermi-dirac distribution

$$Z_r = \sum_{n=0,1} e^{-\beta \cdot n(E_r-\mu)} = 1+e^{-\beta(E_r-\mu)} \quad \& \quad Z = \prod_r Z_r$$

4 Classical Thermodynamics

Zeroth law: if two systems are in equilibrium with a third body then they are in equilibrium with eachother as well.

First law: the amount of work required to change an isolated system from state 1 to 2 is independent of how the work is performed

$$\Delta E = Q + W \quad \rightarrow \quad dE = dQ + dW \quad (dW = -p\,dV)$$

↑ non-work, heat exchange

Second law: Kelvin: heat cannot be perfectly converted to work.
Clausius: heat cannot go from cold to hot without work applied.

quasi-static: lies in equilibrium at all points during a process - reversible.
↳ heat ↔ work
adiabatic: isolated, no heat transfer
isothermal: temp stays the same
Carnot cycle - $\eta = 1 - \frac{Q_C}{Q_H} < 1$ always and is most efficient

$$\eta = 1 - \frac{T_c}{T_H}$$ temperature definition

Entropy $S = \int \frac{dQ}{T}$ $\quad dE = dQ - p\,dV$ & $dS = dQ/T$
$= T\,dS - p\,dV$ → first law

entropy never decreases, reversibility implies equal entropy
& $dQ = 0$ implies $dS = 0$

Third Law: Entropy $\rightarrow 0$ as $T \rightarrow 0$ ($S/N \rightarrow 0$ as $T \rightarrow 0$ & $N \rightarrow \infty$)
→ S is not extensive in ground state

$\therefore C_V = 0$ as $T \rightarrow 0$ (from $\Delta S = \int dT \frac{C_V}{T}$)

5.1 liquid-Gas Phase Transition

(first order → $S = -\frac{\partial F}{\partial T}$ or $V = \frac{\partial G}{\partial p}$ discontinuous)
second order as $T \to T_c$

On either side of the liquid gas phase transition line (small $dp \to \Delta V$)
we have equal $G_{liquid} = G_{gas}$ Gibbs free energy

latent heat of transition $L = T(S_{gas} - S_{liquid})$

$$\frac{dp}{dT} = \frac{L}{T(V_{gas} - V_{liquid})}$$ Clausius-Clapeyron relation

5.2 Ising Model

magnetization $m = \frac{1}{N} \sum_i \langle s_i \rangle = \frac{1}{N\beta} \frac{\partial}{\partial B} \ln(Z)$

or $m = -\frac{1}{N} \frac{\partial F}{\partial B}$