Spring 2017 Statistical Mechanics Comp Equation Sheet
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Sterling's Formula $N! \simeq \sqrt{2\pi N}\, N^N e^{-N} \simeq (N/e)^N$, $\ln(N!) = N\ln N - N$

Microcanonical Ensemble

$P(E) = \frac{1}{\Omega(E)}$, $Z = \sum_E P(E)$

$\frac{1}{T} = \frac{\partial S}{\partial E}$, $E = \sum_E E\,P(E)$

$\frac{\partial S}{\partial T} = \frac{C(T)}{T}$ $\quad \Delta S = \int \frac{C(T)}{T} dT$

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

Canonical Ensemble (Gibbs / Boltzmann)

$Z = \sum_n e^{-\beta E_n}$, $\beta = 1/k_B T$, $P(n) = \frac{1}{Z} e^{-\beta E_n} \Rightarrow \frac{1}{Z}\frac{dZ(x)}{dx}$ s.t. $N(x) = N \cdot P(x)$

$\langle E \rangle = \frac{1}{Z}\sum_n E_n e^{-\beta E_n} = -\frac{\partial}{\partial \beta}\ln(Z)$

$C_V = \frac{dE}{dT}\Big|_V$, $\Delta E^2 = \langle E^2\rangle - \langle E\rangle^2 = -\frac{\partial^2}{\partial\beta^2}\ln(Z) = -\frac{\partial\langle E\rangle}{\partial\beta} = k_B T^2 C_V$

$F = -\frac{1}{\beta}\ln(Z)$

$S = k_B \frac{\partial}{\partial T}(T\ln(Z)) = -\frac{\partial}{\partial T}F$, $P = \frac{\partial}{\partial V}(k_B T \ln(Z)) = -\frac{\partial F}{\partial V}$

$\langle M \rangle = N\langle m\rangle = -\frac{\partial F}{\partial B} \rightarrow \langle m \rangle = \frac{1}{N}\frac{1}{\beta}\frac{\partial}{\partial B}\ln(Z)$ & $\chi = \frac{\partial M}{\partial B}$

Grand Canonical Ensemble

$\mathcal{Z} = \sum_n e^{-\beta(E_n - N_n\mu)} = \prod_i \sum_N e^{-\beta N(E_i - \mu)}$

$N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln(\mathcal{Z})$ = consistency eqn on μ

$\Delta N^2 = \frac{1}{\beta^2}\frac{\partial^2}{\partial\mu^2}\ln(\mathcal{Z})$, $P = -\frac{\partial F}{\partial V}$

$\Phi = F - \mu N = -PV \rightarrow P = -\frac{\Phi}{V}$
$= -\frac{1}{\beta}\ln(\mathcal{Z})$

Potentials

$dE = TdS - PdV + \mu dN$ Energy $\quad E = U = Q + W$

$dF = -SdT - PdV + \mu dN$ helmholtz $\quad F = U - TS$

$dG = -SdT + VdP + \mu dN$ Gibbs $\quad G = U + PV - TS$

$d\Phi = -SdT - PdV - Nd\mu$ grand $\quad \Phi = U - TS + \mu N$

$dH = TdS + VdP + \mu dN$ Enthalpy $\quad H = U + PV$

Sakur-Tetrode Eqn for entropy of a free Ideal gas

$S = \frac{\partial}{\partial T}\left(k_B T \ln\left(\frac{Z_1^N}{N!}\right)\right)$, $Z_1 = \frac{V}{\lambda^3}$ & $\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}} \rightarrow S = Nk_B\left[\ln\left(\frac{V}{N\lambda^3}\right) + \frac{5}{2}\right]$

Virial Expansion (Van der Waals)

Meyer f function of the potential

$P = -\frac{\partial F}{\partial V} = \frac{Nk_BT}{V}\left[1 - \frac{N}{2V}\int d^3r\, f(r) + \cdots\right]$, $f(r) = e^{-\beta V(r)} - 1$

Density of States

$k = P/\hbar$ in general, $\omega = k \cdot c$ for photons

* Be sure to multiply by polarization/degeneracy factor! *

$\sum_n \vec{n} \simeq \int d^3\vec{n} = \frac{1}{(2\pi)^3}\int d^3\vec{k}\, d^3\vec{q} \Rightarrow \frac{V}{(2\pi)^3}\int d^3\vec{k}$ or $\frac{V}{(2\pi\hbar)^3}\int d^3\vec{p} \rightarrow \frac{4\pi V}{(2\pi)^3}\int k^2 dk \cdots = \int g(E)\,dE$ determines $g(E)$ DOS

$E = \hbar\omega \therefore g(E) = \frac{V\omega^2}{\pi^2 c^3}$, $E = \frac{p^2}{2m} \therefore g_{3D}(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$ & $g_{2D}(E) = \frac{Vm}{2\pi\hbar^2}$ & $g_{1D}(E) = \frac{V}{\pi\hbar}\sqrt{\frac{m}{2}}\,E^{-1/2}$

$E_n = \hbar\omega(n_x + n_y + n_z + 3/2) \therefore g_{3D}(E_n) \simeq \frac{4\pi}{(\hbar\omega)^3}E_n^2$ & $E_n = \hbar\omega(n_x + n_y + 1) \therefore g_{2D}(E_n) \simeq \frac{2\pi}{(\hbar\omega)^2}E_n$ & $E_n = \hbar\omega(n + 1/2) \therefore g_{1D}(E_n) \simeq \frac{2}{\hbar\omega}$ (overkill)

$E = (p^2c^2 + m^2c^4)^{1/2} \therefore g_{rel}(E) = \frac{VE}{2\pi^2\hbar^3c^3}(E^2 - m^2c^4)^{1/2}$, $E_{box} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \simeq \frac{\pi^2\hbar^2 n^2}{2mV} \therefore g_{box}(E) = \frac{2}{\pi^2}\left(\frac{2m}{\hbar}\right)^{3/2} V E^{1/2}$

Thermodynamics

0th law: if 2 systems are in equilibrium with a third body then they are in equilibrium with eachother too. There is only one temperature.

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

$\Delta E = Q + W \Rightarrow dE = dQ + dW$ & $dQ = TdS$ & $dW = -PdV|_P$

2nd law: Kelvin: heat cannot be perfectly converted into work
Clausius: heat cannot go from cold to hot without applying work
Shannon: Entropy tends to increase

Since $dS = \frac{dQ}{T}$, if $dQ = 0 \therefore$ reversible

$\lim_{\substack{N\to\infty \\ T\to 0}} \frac{S}{N} = 0$ $\quad \lim_{\substack{N\to\infty \\ T\to 0}} C_V = 0$ from $\Delta S = \int dT \frac{C_V(T)}{T}$

3rd law: Entropy goes to 0 as temperature goes to 0. The heat capacity goes to 0 as temperature goes to 0

Latent Heat $L = T\Delta S_{trans}$ $\quad \frac{dP}{dT} = \frac{L}{T\Delta V_{trans}}$ = Clausius-Clapeyron relation obtained from $dG_{gas} = dG_{liquid}$ at transition

Convenient Formulae

$k_B = 8.62\times10^{-5}\,eV/K$ $\quad \Gamma(N) = (N-1)!$ $\quad \Gamma(1/2) = \sqrt{\pi}$

$k_B = 1.381\times10^{-23}\,J/K$, $N_A = 6.022\times10^{23}$, $R = 8.31\,J/_{mol\,K}$, $n_{FD} = \frac{1}{e^{\beta(E-\mu)}+1}$, $n_{BE} = \frac{1}{e^{\beta(E-\mu)}-1}$, $Z = Tr\left[e^{-\beta\hat{H}}\right]$

$H_{BS} = -\vec{m}\cdot\vec{B} = -\gamma\vec{S}\cdot\vec{B} = -\frac{\hbar\gamma}{2}\vec{\sigma}\cdot\vec{B} \rightarrow$ free then $\vec{\sigma}\cdot\vec{B} \Rightarrow \pm B_z$, else $e^{\vec{r}\cdot\vec{\sigma}} = \mathbb{1}\cosh(|\vec{r}|) + \hat{r}\cdot\vec{\sigma}\sinh(|\vec{r}|)$, also enumerating states is valid

$\sum_n^\infty X = \frac{1}{1-X}$, $\sum_n^N X = \frac{1-X^{N+1}}{1-X}$ for $X < 1$, $\frac{d\tanh(x)}{dx} = 1 - \tanh^2(x) = \text{sech}^2(x)$ $(\sinh^2 x - \cosh^2 x = 1)$

$\int_0^\infty x^n e^{-x/a}dx = n!\,a^{n+1}$ $\quad \int_0^\infty e^{-\alpha x^2}dx = \sqrt{\frac{\pi}{\alpha}}$, $H_{\substack{rotation \\ B\,field}} = \frac{P_\theta^2}{2I} + \frac{P_\phi^2}{2I\sin^2\theta} - mB\cos\theta$

$\int_0^\infty \frac{dx\, x^{N-1}}{z^{-1}e^x - 1} = \Gamma(N)\, g_N(z) \rightarrow z = e^{\beta\mu}$, for $z = 1$ $g_N(1) = \zeta(N) \rightarrow \zeta(1) = \infty$, $\zeta(2) = \frac{\pi^2}{6}$, $\zeta(3) = 1.202$, $\zeta(4) =$

Critical temperature for BEC (from Grand Canonical ensemble with appropriate $\ln\prod_n \rightarrow \int dE\, g(E)$)
occurs when $z = 1 \rightarrow \mu = 0 \rightarrow$ find $N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln(\mathcal{Z})$ at $z = 1$ and yields T_c.

In General for $g(E) = C\cdot E^{\alpha-1}$, $\alpha > 1$ we get (and separate out $n = p = E = 0$ ground state modes, finding $n_{g.s.} = 1 - \left(\frac{T}{T_c}\right)^\alpha$ at $T < T_c$)

$N = \int \frac{dE\, C\, E^{\alpha-1}}{\cdots}\Big| = C\beta^{-\alpha+1-1}\Gamma(\alpha+1-1)\, g\ (z)\Big| = C\Gamma(\alpha)\, g_\alpha(z) \therefore T_c = \left[\frac{N}{C}\frac{1}{\Gamma(\alpha)\zeta(\alpha)}\right]^{1/\alpha}\cdot\frac{1}{k}$

'D Ising Model Chain (B=0, restore for χ calc)

$$H = -J\sum_{\langle ij\rangle}\sigma_i\sigma_j, \quad Z = \sum_{\sigma_n} e^{-\beta H}, \quad e^{\Sigma x} = \Pi e^{x}, \quad \therefore Z = \sum_{\sigma_n}\prod_{\langle i,j\rangle} e^{k\sigma_j\sigma_i} \to e^{k\sigma_i\sigma_j} = \cosh(k)\left(1+\sigma_i\sigma_j\tanh(k)\right)$$

y graphs diagrams $Z = \cosh^N(k)\left(1+\underbrace{\tanh^N(k)}_{N\to\infty,\ =0}\right)$ & $\langle\sigma_0\sigma_r\rangle = \frac{1}{Z}\sum_{\sigma_n}\sigma_0\sigma_n e^{-\beta H} = \tanh^r(k) + \tanh^{N-r}(k) \to 0$ too

$$\chi = \beta\sum_r\langle\sigma_0\sigma_r\rangle = 1 + 2\sum_{r=1}^{\infty}\tanh^r(k) = -1 + 2\sum_{r=0}^{\infty}\tanh^r(k) = -1 + \frac{1}{1-\tanh(k)} = e^{2k} = \chi$$

DNA zipper: $Z = \sum_n^N e^{-\beta n\Delta} = \frac{1-e^{-\beta(N+1)\Delta}}{1-e^{-\beta\Delta}}$ etc... $\langle N\rangle = \frac{-1}{\beta}\frac{d}{d\Delta}\ln(Z)$ = complicated, but not actually hard.