1

$dE = TdS - pdV + \mu dN \quad dG = -SdT + Vdp + \mu\ldots$

$dF = -SdT - PdV + \mu dN \quad d\Phi = -SdT - pdV - Nd\ldots$

microcanonical ensemble $\nearrow S = k_B \ln(\Omega(E))$

definition of T $\quad \frac{1}{T} = \frac{\partial S}{\partial E}$, $P(E) = \frac{1}{\Omega(E)}$

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

Condensed Stat-mech notes

Stirling's formula $\quad N! \simeq \sqrt{2\pi N}\left(\frac{N}{e}\right)^N \simeq \left(\frac{N}{e}\right)^N \quad \therefore \ln(N!) \simeq N\ln N - N$

Gibbs Canonical ensemble $\quad Z = \sum_n e^{-\beta E_n} \quad \beta = 1/k_B T$, $P(n) = \frac{1}{Z} e^{-\beta E_n}$

$\downarrow$ $\quad + N(x) = N \cdot P(x)$

$\langle E \rangle = \frac{1}{Z}\sum_n E_n e^{-\beta E_n} = -\frac{\partial}{\partial\beta}\ln(Z) \qquad P(x) = \frac{1}{Z}\frac{dZ}{dx}$ in general

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

$S = k_B \frac{\partial}{\partial T}(T\ln(Z)) = -\frac{\partial}{\partial T}(F)$, $F = -\frac{1}{\beta}\ln(Z)$ free energy + Gibbs entropy

$M = N\langle m \rangle = -\frac{\partial F}{\partial B} \Rightarrow$ per site $m = \frac{1}{N}\frac{1}{\beta}\frac{\partial}{\partial B}\ln(Z)$, $\chi = \frac{\partial M}{\partial B}$

Sakur tetrode : $S = \frac{\partial}{\partial T}\left(k_B T \ln\left(\frac{Z_1^N}{N!}\right)\right)$ for $Z_1^N = \frac{V^N}{\lambda^{3N}}$, $\lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$

$\therefore S = k_B N\left[\ln\left(\frac{V}{N\lambda^3}\right) + 5/2\right]$ for ideal gas (free).

$\sum_n \vec{n} = \int d^3\vec{n} = \int \frac{d^3\vec{k}}{(2\pi)^3} d^3\vec{q} = \frac{V}{(2\pi)^3}\int d^3\vec{k} = \frac{4\pi V}{(2\pi)^3}\int k^2 dk \cdots = \int g(E)\,dE$

density of states derivation

for classical $V(q)$ potentials this matters

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

Virial expansion : $P = -\frac{\partial F}{\partial V} = \frac{N k_B T}{V}\left[1 - \frac{N}{2V}\int d^3r\, f(r) + \ldots\right]$

of Van der Waals eqn.

$f(r) = e^{-\beta U(r)} - 1$ meyer f function of potential U

(multiply by # of polarizations!)

DOS for non-relativistic free particles $\quad g_3(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$ 3D

$\downarrow$ SHO

$g_3(E) = \frac{4\pi E^2}{(\hbar\omega)^3} \qquad g_2(E) = \frac{Vm}{2\pi\hbar^2}$ 2D

$g_2(E) = \frac{2\pi E}{(\hbar\omega)^2} \qquad g_1(E) = \frac{V}{\pi\hbar}\sqrt{\frac{m}{2}}\, E^{-1/2}$ 1D

$V\omega^2$ / 3D square well $\quad \frac{2}{\ldots}\left(\frac{2m}{\ldots}\right)^{3/2} V E^{\ldots}$

or just pick $\hat{B} = \pm\hat{\sigma}$ — for N spins ≤ 3 or literally count possible spin states

$$H = -\vec{m}\cdot\vec{B} = -\gamma\vec{\sigma}\cdot\vec{B} = -\frac{\hbar}{2}\gamma\,\vec{\sigma}\cdot\vec{B} \rightarrow e^{\vec{r}\cdot\vec{\sigma}} = \mathbb{1}\cdot\cosh(|\vec{r}|) + \hat{r}\cdot\vec{\sigma}\sinh(|\vec{r}|) + Z = Tr\{e^{-\beta\hat{H}}\}$$

Convenient formulas

$$\sum_n^{\infty} x = \frac{1}{1-x} \text{ for } x<1, \quad \sum_n^{N} x = \frac{1-x^{N+1}}{1-x} \text{ for } x<1$$

$$\frac{d\tanh(x)}{dx} = 1-\tanh^2(x) = \operatorname{sech}^2(x)$$

$$\int_0^{\infty} x^n e^{-x/a}\,dx = n!\,a^{n+1} \qquad \int_0^{\infty} e^{-\alpha x^2}\,dx = \sqrt{\frac{\pi}{\alpha}}$$

eqn of state $P = -\frac{\partial F}{\partial V} = \frac{\partial}{\partial V}\left(k_B T\ln(Z)\right)$ for any $Z \propto V^N$ the ideal gas law holds

$$H_{rotation} = T_{rot} + V_{rot} = \frac{P_\theta^2}{2I} + \frac{P_\phi^2}{2I\sin^2\theta} - mB\cos\theta \quad \text{diatomic dipole}$$

$$\int_0^{\infty} \frac{dx\, x^{N-1}}{z^{-1}e^{x}-1} = \Gamma(N)g_N(z) \rightarrow \Gamma(N)g_N(z=1) = \zeta(N)\,\Gamma(N)$$

$z = e^{\beta\mu}$ fugacity; $z=1$ limit; $\Gamma(N) \rightarrow (N-1)!$ or $\Gamma(1/2)=\sqrt{\pi}$

$\zeta(1) = \infty$, $\zeta(2) = \frac{\pi^2}{6} \approx 1.3$, $\zeta(3) = 1.202$, $\zeta(4) = \frac{\pi^4}{90} \approx 1.1$ — Reimann Zeta Function

Critical temperature for BEC requires $z=1$ (can split out $E=0$ mode first) then solve for $N(T_c)\big|_{\mu=0} \rightarrow$ solve for $T_c(N) \rightarrow$ if finite $\therefore$ BEC

In general, for $g(E) = C\cdot E^{\alpha-1}$, $\alpha>1$ we have

$$N = \int \frac{dE\cdot CE^{\alpha-1}}{z^{-1}e^{\beta E}-1}\Bigg|_{z=1} = C\beta^{-\alpha+1-1}\,\Gamma(\alpha-1+1)\,g_{\alpha-1+1}(z)$$

$$= \frac{C\Gamma(\alpha)\,g_\alpha(z)}{\beta_c^{\alpha}} \quad \text{solve for } T_c \rightarrow T_c = \left[\frac{N}{C}\frac{1}{\Gamma(\alpha)\zeta(\alpha)}\right]^{1/\alpha}\frac{1}{k_B}$$

$$+ \; n_{gs} = 1-\left(\frac{T}{T_c}\right)^{\alpha} \text{ for } T<T_c$$

$$n_{FD} = \frac{1}{e^{\beta(E-\mu)}+1}, \quad n_{BE} = \frac{1}{e^{\beta(E-\mu)}-1}$$

$k_B = 1.381\times10^{-23}\,J/K$, $N_A = 6.022\times10^{23}$, $R = 8.31\,J/_{mol\,K}$

Grand Canonical Ensemble + potential . .

$$\mathcal{Z} = \prod_i^{\infty} \sum_n^{N} e^{-\beta n(E_i - \mu)} \qquad N = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln(\mathcal{Z}) \text{ consistency eqn for } \mu$$

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

$$\Phi = F - \mu N = -PV, \quad d\Phi = -S\,dT - p\,dV - N\,d\mu \qquad -PV = \Phi = -k_B T \ln(\mathcal{Z})$$

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

Classical thermodynamics

0th: if 2 systems are in equilibrium with a third body then they are in equilibrium with eachother too,

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

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

2nd: Kelvin: heat cannot be perfectly converted to work

Clausius: heat cannot go from cold to hot without applying work $\qquad dS = \frac{dQ}{T}$

Shannon: Entropy tends to increase $\qquad S = \sum_p p\ln(p) \qquad \therefore dQ = 0 = \text{reversible}$

3rd: Entropy goes to 0 as temperature goes to 0 $\left(\lim_{\substack{N\to\infty \\ T\to 0}} S/N = 0\right)$

The heat capacity goes to 0 as T goes to 0. $\rightarrow$ from $\left(\Delta S = \int dT \frac{C_V(T)}{T}\right)$

Latent heat $\quad L = T\Delta S_{transition} \qquad \frac{dP}{dT} = \frac{L}{T\Delta V_{transition}}$ Clausius-Clapyron relation from $G_{gas} = G_{liquid}$

$+ \ dG = -S\,dT + V\,dP + \mu\ldots$

1D Ising Model Chain $(B=0)$

$$e^{\sum_i x_i} = \prod_i e^{x_i}$$

$$H = -J\sum_{\langle ij\rangle} \sigma_i\sigma_j \qquad \mathcal{Z} = \sum_{\sigma_n} e^{-\beta H} = \sum_{\sigma_n}\prod_{ij} e^{K\sigma_i\sigma_j} \rightarrow e^{K\sigma_i\sigma_j} = \text{Cosh}(K)\cdot(1 + \sigma_i\sigma_j \tanh(\ldots$$

Graph expansion shows $\quad \mathcal{Z} = \cosh^N(K)\,(1 + \underbrace{\tanh^N(K)}_{\to 0 \text{ as } N\to\infty})$

$$\text{then} \quad \langle\sigma_0\sigma_r\rangle = \frac{1}{\mathcal{Z}}\sum_{\sigma_n}\sigma_0\sigma_r e^{-\beta H} = \tanh^r(K) + \underbrace{\tanh^{N-r}(K)}_{\to 0}$$

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

$$= -1 + \frac{2}{\ldots} \ldots \rightarrow \chi = e^{2K}$$