Statistical Mechanics Formula Sheet

Partition functions

- Canonical Ensemble $Q(N,V,T)=\sum_j e^{-\beta E_j(N,V)}$
- Grand canonical Ensemble $Z(V,T,\mu)=\sum_N\sum_j e^{-\beta E_{Nj}(V)+\beta\mu N}$
- Classical theory $Q=\frac{1}{N!h^{sN}}\int\cdots\int e^{-\beta H(p_i,q_i)}\prod_{i=1}^{sN}dp_i\,dq_i$

Thermodynamic Relationships

- $A=-kT\ln Q\,,\quad E=-\frac{\partial\ln Q}{\partial\beta},\quad S=k\ln Q+kT\frac{\partial\ln Q}{\partial T},\quad dE=TdS-pdV+\sum_i\mu_i dN_i$
- $S=k\ln\Omega,\qquad pV=kT\ln Z,\qquad \left(\frac{\partial E}{\partial V}\right)_{T,N}-T\left(\frac{\partial p}{\partial T}\right)_{N,V}=-p$

Energy levels and degeneracy

- Translation $\varepsilon=\frac{h^2}{8ma^2}\left(n_x{}^2+n_y{}^2+n_z{}^2\right)\quad n_x,n_y,n_z=1,2,3\cdots\quad \omega(\varepsilon)=2\pi g\left(\frac{2m}{h^2}\right)^{3/2}V\varepsilon^{1/2}$
- Rotation $\varepsilon_J=\frac{\hbar^2J(J+1)}{2I}\qquad J=0,1,2,\cdots\qquad \omega_J=2J+1$
- Vibration $\varepsilon_n=\left(n+\frac{1}{2}\right)h\nu\qquad n=0,1,2,\cdots\qquad \omega_J=1$

Boltzmann Statistics

- $Q(N,V,T)=\frac{q^N}{N!}$ (N indistinguishable particles) where $q(V,T)=\sum_j e^{-\varepsilon_j/kT}$.

Quantum Statistics

$Z(V,T,\lambda)=\prod_k\left(1\pm\lambda e^{-\beta\varepsilon_k}\right)^{\pm1}$ where + is for fermions and − for bosons.

- $\bar{N}=kT\left(\frac{\partial\ln Z}{\partial\mu}\right)_{V,T}=\lambda\left(\frac{\partial\ln Z}{\partial\lambda}\right)_{V,T}=\sum_k\frac{\lambda e^{-\beta\varepsilon_k}}{1\pm\lambda e^{-\beta\varepsilon_k}},\quad pV=kT\ln Z=\pm kT\sum_k\ln\left[1\pm\lambda e^{-\beta\varepsilon_k}\right]$

  Since $\bar{N}=\sum_k\bar{n}_k,\quad \bar{n}_k=\frac{\lambda e^{-\beta\varepsilon_k}}{1\pm\lambda e^{-\beta\varepsilon_k}}=\frac{1}{1\pm e^{\beta(\varepsilon_k-\mu)}},\quad \bar{E}=\sum_k\bar{n}_k\varepsilon_k$

- Number of valence electrons $N=\int_0^\infty f(\varepsilon)\omega(\varepsilon)d\varepsilon=\int_0^\infty\frac{\omega(\varepsilon)d\varepsilon}{1+e^{\beta(\varepsilon-\mu)}}$ in a strongly

  degenerated fermion gas defines the fermi energy: $\mu_0=\frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}$.

- Heat capacity due to conductance electrons: $C_V = Nk\frac{\pi^2}{2}\frac{kT}{\mu_0} = Nk\frac{\pi^2}{2}\frac{T}{T_F}$.
- Average number of strongly degenerate ideal bosons in the ground state is given by $n_0 = \frac{\lambda}{1-\lambda} = \frac{V}{\Lambda^3}\left(\rho\Lambda^3 - g_{3/2}(1)\right)$. This defines the temperature T_0 where the Bose-Einstein condensation occurs: $\rho\Lambda_0{}^3 = \rho\left(\frac{h^2}{2\pi mkT_0}\right)^{3/2} = g_{3/2}(1)$.

Crystals (3-D crystal consisting of *N* atoms)

- $Q = \prod_{j=1}^{3N}\left(\frac{e^{-h\nu_j/2kT}}{1-e^{-h\nu_j/kT}}\right)e^{-U(\mathbf{0};\rho)/kT}, E = kT^2\left(\frac{\partial \ln Q}{\partial T}\right) = U(\mathbf{0};\rho) + \int_0^\infty\left[\frac{h\nu e^{-h\nu/2kT}}{1-e^{-h\nu/kT}} + \frac{h\nu}{2}\right]g(\nu)\,d\nu$
- Energy in wavenumber space for 1-D crystal, $E = \sum_j \frac{h\nu_j}{e^{\beta h\nu_j}-1} = \frac{Na}{\pi}\int_0^{\pi/a}\frac{h\nu(k)}{e^{\beta h\nu(k)}-1}dk$
- Einstein Theory: $g(\nu) = 3N\delta(\nu-\nu_E)$, $\quad C_V = 3Nk\left(\frac{\Theta_E}{T}\right)^2\frac{e^{-\Theta_E/T}}{\left(1-e^{-\Theta_E/T}\right)^2}$
- Debye Theory: $g(\nu \le \nu_D) = \frac{9N}{\nu_D{}^3}\nu^2$, $\quad C_V = 9Nk\left(\frac{T}{\Theta_D}\right)^3\int_0^{\Theta_D/T}\frac{x^4e^x}{\left(e^x-1\right)}dx = 3NkD\left(\frac{T}{\Theta_D}\right)$

Physical Constants:

$m_e = 9.11\times10^{-31}$ kg, $\quad m_p = 1.67\times10^{-27}$ kg, $\quad k = 1.38\times10^{-23}$ J/K, $\quad h = 6.63\times10^{-34}$ J s

1 eV $=1.60\times10^{-19}$ J, $\quad$ 1 Pa $=1$ N/m^2 $= 9.87\times10^{-6}$ atm, $\quad \sigma = 5.67\times10^{-8}\,\mathrm{Wm^{-2}K^{-4}}$

$N_A = 6.022\times10^{23}$ mol^{-1}

Math Formulae:

$\ln N! \approx N\ln N - N$, $\quad \sum_{k=0}^{\infty} ar^k = \frac{a}{1-r}$, $\quad \left(x_1 + x_2 + \cdots + x_r\right)^N = \sum_{N_1=0}\cdots\sum_{N_r=0}\frac{N!}{\prod_i^r N_i!}x_1^{N_1}\cdots x_r^{N_r}$

$$\int_0^\infty x^n e^{-ax^2}dx = \begin{cases} \frac{1\cdot3\cdot5\cdots(n-1)}{2(2a)^{n/2}}\left(\frac{\pi}{a}\right)^{1/2} & \text{even } n \\ \frac{1}{2a^{(n+1)/2}}\Gamma\left(\frac{n+1}{2}\right) & \text{odd } n \end{cases},$$

$$\Gamma(x) = \int_0^\infty e^{-t}t^{x-1}dt, \quad \Gamma(x+1) = x\Gamma(x), \quad \Gamma\left(\tfrac{1}{2}\right) = \sqrt{\pi}$$

$\frac{d}{dx}\sin^{-1}u = \frac{1}{\sqrt{1-u^2}}\frac{du}{dx}$ where $-\frac{\pi}{2} < \sin^{-1}u < \frac{\pi}{2}$, $\quad \frac{1}{1-x} = \sum_{i=0}^{\infty}x^i$ where $x < 1$