

Formula Sheet of Statistical Mechanics

Ch. 1 Review

1. Lagrangian equation and Hamilton's equation

$$\frac{dL}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) = \frac{\partial L}{\partial q_j}, \quad p_j = \frac{\partial L}{\partial \dot{q}_j}$$

$$\frac{\partial H}{\partial p_j} = \dot{q}_j$$

$$\frac{\partial H}{\partial q_j} = -\dot{p}_j$$

2. Energy Levels of some quantum systems

a) 1-D infinite well: $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$, $e_n = \frac{h^2 n^2}{8ma^2}$.

b) 1-D oscillator: $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2$, $e_n = \left(n + \frac{1}{2}\right) \hbar \omega$.

c) Rigid rotor: $H = -\frac{\hbar^2}{2I} \left\{ \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \theta} \left(\sin^2 \theta \frac{\partial}{\partial \theta} \right) + \left(\frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \right\}$, $e_n = J(J+1) \frac{\hbar^2}{2I}$.

3. Calculation of Degeneracy

$$w(\mathbf{e}) d\mathbf{e} = \frac{\Phi(\mathbf{e})}{\mathbf{e}} d\mathbf{e}$$

3-D infinite well: $\mathbf{e} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \rightarrow n_x^2 + n_y^2 + n_z^2 = \frac{8ma^2 \mathbf{e}}{h^2} = R^2$

$$\rightarrow \Phi(\mathbf{e}) = \frac{1}{8} \left(\frac{4\mathbf{p}}{3} R^2 \right) = \frac{\mathbf{p}}{6} \left(\frac{8ma^2 \mathbf{e}}{h^2} \right)^{3/2}$$

4. Thermodynamics equations

$$dE = TdS - pdV + \sum_j \mathbf{m}_j dN_j, \quad dH = TdS + Vdp + \sum_j \mathbf{m}_j dN_j$$

$$dA = -SdT - pdV + \sum_j \mathbf{m}_j dN_j, \quad dG = -SdT + Vdp + \sum_j \mathbf{m}_j dN_j$$

5. Useful mathematical formula

$$nN! = N \ln N - N, \quad (x_1 + x_2 + \dots + x_r)^N = \sum_{N_1=0}^N \dots \sum_{N_r=0}^N \frac{N! x_1^{N_1} \dots x_r^{N_r}}{\prod_i N_i!}$$

$$I_n = \int_0^\infty x^n e^{-ax^2} dx = \begin{cases} \frac{1 \cdot 3 \cdot 5 \dots (n-1)}{2(2a)^{n/2}} \left(\frac{\mathbf{p}}{a} \right)^{1/2}, & n = \text{even} \\ \frac{\Gamma\left(\frac{n+1}{2}\right)}{2a^{(n+1)/2}}, & n = \text{odd} \end{cases}$$

6. Constants: Stefan-Boltzman constant $\sigma = 5.67 \times 10^{-8} \text{W/m}^2 \text{K}^4$,

Bohr Magneton: $9.273 \times 10^{-21} \text{erg gauss}^{-1}$

Ch. 2 The Canonical Ensemble

$$W(a) = \frac{A!}{\prod_k a_k!}$$

$$P_j = \frac{\bar{a}_j}{A} = \frac{1}{A} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)} = \frac{a_j^*}{A}$$

$$\frac{\mathcal{I}}{\mathcal{I} a_j} \left\{ \lambda n W(a) - \mathbf{a} \sum_k a_k - \mathbf{b} \sum_k a_k E_k \right\} = 0$$

$$p_j = - \left(\frac{\partial E_j}{\mathcal{I} V} \right)_N$$

$$\bar{p} = \sum_j p_j P_j = - \frac{\sum_j \left(\frac{\partial E_j}{\mathcal{I} V} \right) e^{-b \mathbf{e}_j}}{\sum_j e^{-b \mathbf{e}_j}}$$

$$\left(\frac{\mathcal{I} \bar{E}}{\mathcal{I} V} \right)_{N, \mathbf{b}} = -\bar{p} + \mathbf{b} \bar{E} \bar{p} - \mathbf{b} \bar{E} \bar{p}$$

$$\left(\frac{\mathcal{I} \bar{E}}{\mathcal{I} V} \right)_{N, \mathbf{b}} + \mathbf{b} \left(\frac{\mathcal{I} \bar{p}}{\mathcal{I} \mathbf{b}} \right)_{N, V} = -\bar{p}$$

$$\left(\frac{\mathcal{I} \bar{p}}{\mathcal{I} \mathbf{b}} \right)_{N, V} = \bar{E} \bar{p} - \bar{E} p$$

$$\left(\frac{\mathcal{I} E}{\mathcal{I} V} \right)_{T, N} - T \left(\frac{\mathcal{I} p}{\mathcal{I} T} \right)_{N, V} = -p$$

$$W(a, b) = \frac{A!}{\prod_j a_j!} \frac{B!}{\prod_k b_k!}$$

$$S = \frac{\bar{E}}{T} + k \lambda n Q + \text{const}$$

$$d\bar{E} = \sum_j E_j d p_j + \sum_j p_j d E_j = d\mathbf{q}_{rev} - d\mathbf{w}_{rev}$$

$$E = kT^2 \left(\frac{\mathcal{I} \lambda n Q}{\mathcal{I} T} \right)_{N, V}$$

$$p = kT \left(\frac{\mathcal{I} \lambda n Q}{\mathcal{I} V} \right)_{N, T}$$

$$S = kT \left(\frac{\mathcal{I} \lambda n Q}{\mathcal{I} T} \right)_{N, V} + k \lambda n Q$$

$$A(N, V, T) = -kT \lambda n Q(N, V, T)$$

Ch. 3 Formula Table

Microcanonical ensemble, $\Omega(N, V, E)$ = degeneracy

$$S = k \ln \Omega$$

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mathbf{m}}{T} dN$$

$$\frac{1}{kT} = \left(\frac{\partial \ln \Omega}{\partial E} \right)_{N, V}$$

$$\frac{p}{kT} = \left(\frac{\partial \ln \Omega}{\partial V} \right)_{N, E}$$

$$\frac{\mathbf{m}}{kT} = - \left(\frac{\partial \ln \Omega}{\partial N} \right)_{V, E}$$

Canonical ensemble, $Q(N, V, T) = \sum_j e^{-bE_j(N, V)}$

$$A = -kT \ln Q$$

$$dA = -SdT - pdV + \mathbf{m}dN$$

$$S = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V}$$

$$p = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N, T}$$

$$\mathbf{m} = -kT \left(\frac{\partial \ln Q}{\partial N} \right)_{V, T}$$

$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V}$$

Grand canonical ensemble, $\Xi(V, T, \mathbf{m}) = \sum_N \sum_j e^{-bE_j} e^{\frac{\mathbf{m}V}{kT}}$

$$pV = kT \ln \Xi$$

$$d(pV) = SdT + Nd\mathbf{m} + pdV$$

$$S = k \ln \Xi + kT \left(\frac{\partial \ln \Xi}{\partial T} \right)_{V, \mathbf{m}}$$

$$N = kT \left(\frac{\partial \ln \Xi}{\partial \mathbf{m}} \right)_{V, T}$$

$$p = kT \left(\frac{\partial \ln \Xi}{\partial V} \right)_{\mathbf{m}, T} = kT \frac{\ln \Xi}{V}$$

$$E = - \left(\frac{\partial \ln \Xi}{\partial \mathbf{b}} \right)_{V, g}$$

Isothermal-isobaric ensemble, $\Delta(N, T, p) = \sum_E \sum_V \Omega(N, V, E) e^{-bE_j} e^{\frac{pV}{kT}}$

$$G = -kT \ln \Delta$$

$$dG = -SdT + Vdp + \mathbf{m}dN$$

$$S = k \ln \Delta + kT \left(\frac{\partial \ln \Delta}{\partial T} \right)_{N, p}$$

$$V = -kT \left(\frac{\partial \ln \Delta}{\partial p} \right)_{N, T}$$

$$\mathbf{m} = -kT \left(\frac{\partial \ln \Delta}{\partial N} \right)_{T, p}$$

Ch. 4 Boltzmann, Fermi-Dirac and Bose-Einstein Statistics

1. Boltzmann Statistics

Partition function for a single particle : $q(V, T) = \sum_i e^{-e_i/kT}$

Partition Function for the system : $Q(N, V, T) = (q(V, T))^N$ or $q^N / N!$

Probability for particles in jth state : $\frac{\bar{n}_j}{N} = \frac{e^{-e_j/kT}}{q}$

2. Fermi-Dirac & Bose-Einstein Statistics: (Grand Canonical Ensemble)

$$\begin{aligned} \Xi(V, T, \mathbf{m}) &= \sum_{n=0}^{\infty} I^N \sum_{\{n_k\}}^* e^{-b \sum_i e_i n_i} = \sum_{n=0}^{\infty} \sum_{\{n_k\}}^* \prod_k (I e^{-be_k})^k \\ &= \sum_{n_1=0}^{n_1^{\max}} \sum_{n_2=0}^{n_2^{\max}} \prod_k (I e^{-be_k})^k = \prod_k \sum_{n_k=0}^{n_k^{\max}} (I e^{-be_k})^k \end{aligned}$$

where $I = e^{bm}$, F-D : $n_k^{\max} = 1$, B-E : $n_k^{\max} = \infty$

$$\therefore \Xi_{FD} = \prod_k (1 \pm I e^{-be_k})^{\pm 1}$$

$$\bar{N} = \sum_k \bar{n}_k = kT \left(\frac{\partial \ln \Xi}{\partial m} \right)_{V, T} = \sum_k \frac{I e^{-be_k}}{1 \pm I e^{-be_k}}, \quad \bar{n}_k = \frac{I e^{-be_k}}{1 \pm I e^{-be_k}}$$

$$\bar{E} = \sum_k \bar{n}_k e_k = \sum_k \frac{I e^{-be_k} e_k}{1 \pm I e^{-be_k}}, \quad pV = kT \ln \Xi = \pm kT \sum_k \ln(1 \pm I e^{-be_k})$$

3. At high T & low density, F-D & B-E statistics goes to Boltzmann

4. Math formula : $\sum_{j=0}^{\infty} x^j = (1-x)^{-1}$ where $x < 1$

Ch. 5 Ideal Monatomic Gas

$$H = H_{trans} + H_{elect} + H_{nucl}$$

$$q_{trans} = \left(\sum_{n=1}^{\infty} \exp\left(-\frac{bh^2 n^2}{8ma^2}\right) \right)^3$$

$$q_{trans} = \frac{V}{\Lambda^3}, \quad \text{where} \quad \Lambda = \left(\frac{h^2}{2pmkT} \right)^{1/2}$$

$$q_{elect} = \sum_i w_{elect-i} e^{-be_i}$$

$$q_{nucl} = w_{nucl}$$

Ch. 6 Ideal Diatomic Gas

$$1. H = H_{trans} + H_{rot} + H_{vib} + H_{elec} + H_{nucl}, \quad E = E_{trans} + E_{rot} + E_{vib} + E_{elec} + E_{nucl}$$

$$2. Q(V, N, T) = \frac{(q_{trans} q_{rot} q_{vib} q_{elec} q_{nucl})^N}{N!}$$

$$3. E_{rot, J} = \frac{\eta^2 J(J+1)}{2I} = BJ(J+1)$$

$$a) \text{ For heteronuclear molecule, } q_{rot} = \sum_{J=0}^{\infty} (2J+1) e^{-BJ(J+1)/kT} = \sum_{J=0}^{\infty} (2J+1) e^{-\Theta_r J(J+1)/T}$$

$$b) \text{ At } \Theta_r \ll T, q_{rot} \approx \frac{8p^2 kT}{wh^2}, w=1 \text{ for hetero-, } 2 \text{ for homo-nuclear dia-molecule}$$

$$c) f_n = \frac{N_J}{N} \propto (2J+1) e^{-\Theta_r J(J+1)/T}$$

$$d) J_{max} = \sqrt{\frac{kT}{2B}}$$

$$5. E_{vib} = (n + \frac{1}{2}) h\nu \quad n=0, 1, 2, \dots, v = \frac{1}{2p} \sqrt{\frac{k}{m}}$$

$$a) q_{vib} = \sum_n e^{-\beta \epsilon_n} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}}$$

$$b) f_n \propto e^{-bh\nu(n+1/2)}$$

Ch. 7 Classical Statistical Mechanics

1. Formulas for classical and indistinguishable system

$$q = \sum_j e^{-be_j} \rightarrow \frac{1}{h^s} \int \dots \int e^{-bH} \prod_{j=1}^s dp_{ji} dq_{ji} \quad (7-8)$$

$$Q = \frac{q^N}{N!} = \sum_j e^{-bE_j} \rightarrow \frac{1}{N! h^{Ns}} \int \dots \int e^{-bH(p,q)} dp dq. \quad (7-10)$$

Where s is the degree of freedom of the molecular.

2. Examples:

$$a) \text{ The translation motion, } H = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

$$q_{class} \sim \frac{1}{h^3} \int \cdot \int \exp\left\{-\frac{\mathbf{b}(p_x^2 + p_y^2 + p_z^2)}{2m}\right\} dp_x dp_y dp_z dx dy dz = \frac{V}{h^3} \left\{ \int_{-\infty}^{\infty} e^{-bp^2/2m} dp \right\}^3 = \left(\frac{2\mathbf{p}mkT}{h^2}\right)^{3/2} V$$

b) The rigid rotor, $H = \frac{1}{2I}(p_q^2 + \frac{p_f^2}{\sin^2 q})$

$$q_{rot} \sim \frac{1}{h^2} \int_{-\infty}^{\infty} \int dp_q dp_f \int_0^{2\pi} df \int_0^{\pi} dq e^{-bH} = \frac{8\mathbf{p}IkT}{h^2}$$

c) The classical harmonic oscillator, $H = \frac{p^2}{2m} + \frac{k}{2}x^2$

$$q_{vib} \sim \frac{1}{h} \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx e^{-bH} = \frac{2\mathbf{p}kT}{h} \left(\frac{m}{k}\right)^{1/2} = \frac{kT}{nh}, \quad \mathbf{n} = \frac{1}{2\mathbf{p}} \left(\frac{k}{m}\right)^{1/2}$$

Chapter 10 Quantum Statistics

$$\Xi(V, T, I) = \prod_k \left(1 \pm I e^{-\mathbf{b}e_k} \right)^{\pm 1}, \quad \text{where } \mathbf{b} = \frac{1}{kT} \text{ and } I = e^{\mathbf{b}m}$$

$$N = \sum_k \frac{I e^{-\mathbf{b}e_k}}{1 \pm I e^{-\mathbf{b}e_k}}$$

$$\bar{n}_k = \frac{I e^{-\mathbf{b}e_k}}{1 \pm I e^{-\mathbf{b}e_k}}$$

$$E = \sum_k \frac{I e_k e^{-\mathbf{b}e_k}}{1 \pm I e^{-\mathbf{b}e_k}}$$

(I) Weakly Degenerate Fermi - Dirac Gas

$$N = \sum_k \frac{I e^{-\mathbf{b}e_k}}{1 \pm I e^{-\mathbf{b}e_k}}$$

$$PV = kT \sum_k \ln \left(1 + I e^{-\mathbf{b}e_k} \right)$$

$$e_{n_x, n_y, n_z} = \frac{h^2}{8mV^{2/3}} \left(n_x^2 + n_y^2 + n_z^2 \right) \text{ where } a^2 = V^{2/3} \text{ and } n_x, n_y, n_z = 1, 2, \dots$$

$$N = 2\mathbf{p} \left(\frac{2m}{h^2} \right)^{3/2} V \int_0^{\infty} \frac{I e^{1/2} e^{-\mathbf{b}e} de}{1 + I e^{-\mathbf{b}e}}$$

$$PV = 2pkT \left(\frac{2m}{h^2} \right)^{3/2} V \int_0^\infty \mathbf{e}^{1/2} \ln(1 + I e^{-b\mathbf{e}}) d\mathbf{e}$$

$$\frac{N}{V} = \mathbf{r} = \frac{1}{\Lambda^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} I^l}{l^{3/2}}$$

$$\frac{P}{kT} = \frac{1}{\Lambda^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} I^l}{l^{5/2}} \quad \text{where } \Lambda = \left(\frac{h^2}{2pmkT} \right)^{1/2}$$

$$I = a_0 + a_1 \mathbf{r} + a_2 \mathbf{r}^2 + \dots$$

$$a_0 = 0, a_1 = \Lambda^3, a_2 - \frac{a_1^2}{2^{3/2}} = 0, a_3 - \frac{a_1 a_2}{2^{1/2}} + \frac{a_1^3}{2^{3/2}} = 0, \dots$$

$$I = \mathbf{r} \Lambda^3 + \frac{1}{2^{3/2}} (\mathbf{r} \Lambda^3)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}} \right) (\mathbf{r} \Lambda^3)^3 + \dots$$

$$\frac{P}{kT} = \mathbf{r} + \frac{\Lambda^3}{2^{5/2}} \mathbf{r}^2 + \left(\frac{1}{8} - \frac{2}{3^{5/2}} \right) \Lambda^6 \mathbf{r}^3 + \dots$$

$$\frac{P}{kT} = \mathbf{r} + B_2(T) \mathbf{r}^2 + B_3(T) \mathbf{r}^3 + \dots$$

$$E = \frac{3}{2} V kT \frac{1}{\Lambda^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} I^l}{l^{5/2}} = \frac{3}{2} V kT \left(1 + \frac{\Lambda^3}{2^{5/2}} \mathbf{r} + \dots \right)$$

$$\bar{n}_k = \frac{I e^{-b\mathbf{e}_k}}{1 + I e^{-b\mathbf{e}_k}} = \frac{1}{1 + e^{-b(\mathbf{e}_k - m)}}$$

(II) Strongly Degenerate Ideal F - D Gas

$$\bar{n}_k = \frac{I e^{-b\mathbf{e}_k}}{1 + I e^{-b\mathbf{e}_k}} = \frac{1}{1 + e^{-b(\mathbf{e}_k - m)}}$$

$$f(\mathbf{e}) = \frac{1}{1 + e^{-b(\mathbf{e}_k - m)}}$$

$$w(\mathbf{e}) d\mathbf{e} = 4p \left(\frac{2m}{h^2} \right)^{3/2} V \mathbf{e}^{1/2} d\mathbf{e}$$

$$\mathbf{m}_0 = \frac{h^2}{2m} \left(\frac{3}{8p} \right)^{2/3} \left(\frac{N}{V} \right)^{2/3}$$

$$\text{For } \mathbf{h} = (\mathbf{b}\mathbf{m}_0)^{-1} < 1, \quad \mathbf{m} = \mathbf{m}_0 \left[1 - \frac{\mathbf{p}^2}{12} \mathbf{h}^2 + \dots \right]$$

$$E = E_0 \left[1 + \frac{5\mathbf{p}^2}{12} \mathbf{h}^2 + \dots \right]$$

$$C_V = \left(\frac{\mathcal{I}E}{\mathcal{I}T} \right)_V = \frac{\mathbf{p}^2}{2} Nk \left(\frac{T}{T_F} \right)$$

(III) Weakly Degenerate Ideal B - E Gas

$$N = \sum_k \frac{I e^{-be_k}}{1 - I e^{-be_k}} \Rightarrow N = \frac{I e^{-be_k}}{1 - I e^{-be_k}} + 2\mathbf{p} \left(\frac{2m}{h^2} \right)^{3/2} V \int_{e>e_0}^{\infty} \frac{I e^{1/2} e^{-be_k} de}{1 - I e^{-be_k}}$$

$$PV = -kT \sum_k \ln(1 - I e^{-be_k})$$

$$\mathbf{r} = \frac{N}{V} = 2\mathbf{p} \left(\frac{2m}{h^2} \right)^{3/2} \int_{e>e_0}^{\infty} \frac{I e^{1/2} e^{-be_k} de}{1 - I e^{-be_k}} + \frac{I}{V(1-I)}$$

$$\frac{P}{kT} = -2\mathbf{p} \left(\frac{2m}{h^2} \right)^{3/2} \int_{e>e_0}^{\infty} e^{1/2} \ln(1 - I e^{-be_k}) de - \frac{1}{V} \ln(1 - I)$$

$$\mathbf{r} = \frac{1}{\Lambda^3} g_{3/2}(I) \quad \text{and} \quad \frac{P}{kT} = \frac{1}{\Lambda^3} g_{5/2}(I), \quad \text{where } g_n(I) = \sum_{l=1}^{\infty} \frac{I^l}{l^n}$$

$$\frac{P}{\mathbf{r}kT} = 1 - \frac{\Lambda^3}{2^{5/2}} \mathbf{r} + \dots$$

$$E = \frac{3}{2} NkT \left(1 - \frac{\Lambda^3}{2^{5/2}} \mathbf{r} + \dots \right)$$

(IV) Strongly Degenerate Ideal B - E Gas

$$\mathbf{r} = \frac{1}{\Lambda^3} g_{3/2}(I) + \frac{I}{V(1-I)}$$

$$\frac{P}{kT} = \frac{1}{\Lambda^3} g_{5/2}(I) - \frac{1}{V} \ln(1 - I)$$

$$\bar{n}_0 = \frac{I}{(1-I)}, \quad 0 \leq I < 1 \text{ for B - E and } 0 \leq I < \infty \text{ for F - D}$$

$$\mathbf{r}\Lambda_0^3 = \mathbf{r} \left(\frac{h^2}{2\mathbf{p}mkT_0} \right)^{3/2} = g_{3/2}(1) = 2.612$$

$$\frac{\bar{n}_0}{N} = 1 - \left(\frac{T}{T_0} \right)^{3/2} \quad \text{for } T < T_0$$

$$\frac{\bar{n}_0}{N} = 0 \quad \text{for } T > T_0$$

B-E Condensation

$$\frac{\bar{n}_0}{N} = 1 - \frac{r_0}{r}, \quad \text{for } r < r_0; \quad \frac{\bar{n}_0}{N} = 0, \quad \text{for } r > r_0$$

$$\frac{P}{kT} = \frac{1}{\Lambda^3} g_{5/2}(I) \text{ for } r < r_0; \quad \frac{P}{kT} = 1.342 \text{ for } r > r_0$$

$$\frac{E}{N} = \frac{3}{2} \frac{kTV}{\Lambda^3} g_{5/2}(I) \text{ for } T > T_0; \quad \frac{E}{N} = \frac{3}{2} \frac{kTV}{\Lambda^3} g_{5/2}(1) \text{ for } T < T_0$$

$$\frac{C_V}{Nk} = \frac{15}{4} \frac{V}{\Lambda^3} g_{5/2}(I) - \frac{9}{4} \frac{g_{3/2}(I)}{g_{1/2}(I)} \text{ for } T > T_0$$

$$\frac{C_V}{Nk} = \frac{15}{4} \frac{V}{\Lambda^3} g_{5/2}(1) \text{ for } T < T_0$$

Black-Body Radiation

$$k = \frac{n\mathbf{p}}{L}, \quad n = 1, 2, \dots \quad \Phi(k) = \frac{1}{8} \times \frac{4}{3} \mathbf{p} R^3 \quad \text{where } R = \frac{kL}{\mathbf{p}}$$

$$w(k)dk = \frac{d\Phi(k)}{dk} dk$$

$$Q(V, T) = \prod_k \left(\sum_{n=0}^{\infty} e^{-be_k n} \right) = \prod_k \frac{1}{1 - e^{-be_k}}$$

$$E = \frac{\mathbf{p}^2 V (kT)^4}{15(\eta c)^3} \quad R = sT^4 \quad P = kT \left(\frac{\mathcal{I}Q}{\mathcal{I}V} \right)_T = \frac{\mathbf{p}^2 (kT)^4}{15(\eta c)^3}$$

Ch. 11 Crystals

1. General Treatment for Monatomic Crystal:

$$U(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = U(0, 0, \dots, 0) + \frac{1}{2} \sum_{i,j} k_{ij} \mathbf{x}_i \mathbf{x}_j + \Lambda, \quad \text{where } k_{ij} = \left(\frac{\mathcal{I}^2 U}{\mathcal{I}_i \mathcal{I}_j} \right)_0$$

The complete partition function:

$$Q\left(\frac{V}{N}, T\right) = e^{-U(0; \mathbf{r})/kT} \prod_{j=1}^{3N} q_{vib,j}, \quad \text{where } q_{vib,j} = \frac{e^{-hn_j/2kT}}{1 - e^{-hn_j/kT}}$$

$$- \ln Q = \frac{U(0; \mathbf{r})}{kT} + \int_0^{\infty} \left[\ln(1 - e^{-hn/kT}) + \frac{hn}{2kT} \right] g(\mathbf{n}) d\mathbf{n}, \quad \text{where } \int_0^{\infty} g(\mathbf{n}) d\mathbf{n} = 3N$$

$$E = U(0; \mathbf{r}) + \int_0^{\infty} \left[\frac{hne^{-hn/kT}}{(1 - e^{-hn/kT})} + \frac{hn}{2} \right] g(\mathbf{n}) d\mathbf{n}$$

$$C_n = k \int_0^\infty \frac{(hn/kT)^2 e^{-hn/kT} g(\mathbf{n}) d\mathbf{n}}{(1 - e^{-hn/kT})^2}$$

2. The Einstein Theory:

$$g(\mathbf{n}) = 3N d(\mathbf{n} - \mathbf{n}_E)$$

$$C_v = 3Nk \left(\frac{hn_E}{kT} \right)^2 \frac{e^{-hn_E/kT}}{(1 - e^{-hn_E/kT})^2}$$

3. The Debye Theory:

$$\frac{\bar{\omega}}{k} = \frac{\mathbf{p}}{L} \bar{n}, \quad g(\mathbf{n}) d\mathbf{n} = \frac{4\mathbf{p}V\mathbf{n}^2}{v_0^3} d\mathbf{n}, \quad \text{where } \frac{3}{v_0^2} = \frac{1}{v_t^2} + \frac{1}{v_l^2}$$

$$\mathbf{n}_D = \left(\frac{3N}{4\mathbf{p}V} \right)^{1/3} v_0, \quad g(\mathbf{n}) d\mathbf{n} = \frac{9N}{\mathbf{n}_D^3} \mathbf{n}^2 d\mathbf{n}, \quad \text{for } 0 \leq \mathbf{n} \leq \mathbf{n}_D$$

$$C_v = 9Nk \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \equiv 3NkD \left(\frac{T}{\Theta_D} \right), \quad \Theta_D = \frac{hn_D}{k}$$

4. Monatomic lattice dynamics:

$$H = \sum_{j=1}^N \frac{m}{2} \mathbf{x}_j^2 + \sum_2 \frac{k}{2} (\mathbf{x}_j - \mathbf{x}_{j-1})^2; \quad \mathbf{x}_j = e^{i nka - i \omega t}$$

$$\omega^2 = \frac{4k}{m} \sin^2 \left(\frac{ka}{2} \right)$$

$$E = \sum_j \frac{\eta \omega}{e^{b\eta \omega_j} - 1} = \frac{N\mathbf{p}}{a} \int_0^{p/a} \frac{\eta \omega(k) dk}{e^{b\eta \omega} - 1} = \frac{2N}{\mathbf{p}} \int_0^{\omega_{\max}} \frac{\eta \omega d\omega}{(e^{b\eta \omega} - 1)(\omega_{\max}^2 - \omega^2)^{1/2}}$$

$$g(\mathbf{n}) = \frac{2N}{\mathbf{p}} \frac{1}{(\mathbf{n}_{\max}^2 - \mathbf{n}^2)^{1/2}}; \quad \text{c.f. 1-D case: } g(\mathbf{n}) = \frac{Na}{\mathbf{p}} \frac{1}{dn/dk}$$

5. Diatomic lattice dynamics:

$$H = \sum_{j=1}^N \left(\frac{m_1}{2} \mathbf{x}_{2j}^2 + \frac{m}{2} \mathbf{x}_{2j-1}^2 \right) + \frac{k}{2} \sum_{j=1}^N \left\{ (\mathbf{x}_{2j} - \mathbf{x}_{2j-1})^2 + (\mathbf{x}_{2j+1} - \mathbf{x}_{2j})^2 \right\}$$

$$\omega = \frac{f}{\mathbf{m}} \left\{ 1 \pm \left(1 - \frac{4m_1 m_2 \sin^2 \left(\frac{ka}{2} \right)}{m_1 + m_2} \right)^{1/2} \right\}, \quad \text{where } a \text{ is the crystal constant.}$$

Phonons:

$$\bar{n}_j = \frac{1}{e^{be_j} - 1}; \quad \bar{E} = E_0 + \int_0^\infty \frac{g(\mathbf{n}) h \mathbf{n} d\mathbf{n}}{e^{b\mathbf{n}} - 1}$$

Point Effects:

$$\text{Schottky defect: } \bar{n} \approx N e^{-e_s/kT}$$

$$\text{Frenkel defect: } \bar{n} \approx (NN')^{1/2} e^{-e_f/2kT}$$

$$\text{Passing over prob.: } p \approx n e^{-e/kT}$$

$$\text{Diffusion: } j = -pa^2 \frac{\mathcal{J}n}{\mathcal{J}x} = -D \frac{\mathcal{J}n}{\mathcal{J}x}; \quad D = pa^2 \approx na^2 e^{-e/kT}$$

CH. 13 Ideal System in E and M Fields

Electric field:

$$\mathbf{e}(E_z^*) = -\mathbf{m}E_z^* \cos q - \frac{1}{2} \mathbf{a}E_z^{*2}$$

$$q_{elec} = \frac{1}{4\mathbf{p}} \int_0^{2\mathbf{p}} d\mathbf{f} \int_0^{\mathbf{p}} \exp(-\mathbf{e}(E_z^*)/KT) \sin q d\mathbf{q} = \exp(\mathbf{a}E_z^{*2}/2KT) * \frac{\text{Sinh}(\mathbf{m}E_z^*/KT)}{\mathbf{m}E_z^*/KT}$$

$$\overline{M_z} = N \overline{\mathbf{m}_z} = KT(\partial \ln Q / \partial E_z^*)_{N,V,T} \approx N(\mathbf{a} + \mathbf{m}^2/3KT)E_z^* \text{ --- } \mathbf{a}: \text{ polarizability}$$

$$P_z = \frac{\overline{M_z}}{V} = \frac{\mathbf{e}-1}{4\mathbf{p}} E_z$$

Gas:

$$E_z^* = \mathbf{e}E_z$$

$$\frac{\mathbf{e}-1}{\mathbf{e}} = 4\mathbf{p}r \left(\mathbf{a} + \frac{\mathbf{m}^2}{3KT} \right)$$

Liquid:

$$E_z^* = E_z + 4\mathbf{p}P_z/3$$

$$\frac{\mathbf{e}-1}{\mathbf{e}+2} = \frac{4\mathbf{p}r}{3} \left(\mathbf{a} + \frac{\mathbf{m}^2}{3KT} \right)$$

Magnetic field:

$$\mathbf{e}(B_z^*) = g\mathbf{b}_0 B_z^* M_j \quad , (-j \leq M_j \leq j, \quad \mathbf{b}_0 = |e|\hbar/2mc)$$

$$q_{meg} = \sum_{M_j=-j}^{+j} \exp(-\mathbf{e}(B_z^*)/KT) = \left(\frac{\text{Sinh}[(2j+1)y/2]}{\text{Sinh}(y/2)} \right) \quad , (y = g\mathbf{b}_0 B_z^*/KT)$$

$$\overline{M_z} = N \overline{\mathbf{m}_z} = KT(\partial \ln Q / \partial B_z^*)_{N,V,T} = Ng^2 \mathbf{b}_0^2 J(J+1)B_z^*/3KT \quad , (B_z^* = B_z)$$

$$\mathbf{c} = \overline{M_z}/B_z \text{ --- magnetic susceptibility}$$