1 Definitions and Fundamentals

$\beta \equiv \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N} = \frac{1}{k_\mathrm{B} T}$

$\epsilon \equiv \hbar\omega$

Expectation value: $\langle X(E)\rangle = \int_{-\infty}^{\infty} \varphi(E) X(E)\, dE$

Stirling approximation: $\ln N! \approx N(\ln N - 1) \quad N \gg 1$

Dirac delta: $\delta(x) = \begin{cases} +\infty & x = 0 \\ 0 & x \neq 0 \end{cases}$

$\{\forall \epsilon > 0\} : \int_{x_0-\epsilon}^{x_0+\epsilon} \delta(x - x_0)\, dx = 1$

$\Gamma(n) \equiv (n-1)! \qquad n \in \mathbb{N}$

$\mathscr{H}(\boldsymbol{q}, \boldsymbol{P}) \equiv E_\mathrm{p}(\boldsymbol{q}) + E_\mathrm{k}(\boldsymbol{P}) = E_\mathrm{p}(\boldsymbol{q}) + \sum_{i=1}^{N} \frac{|\vec{P}_i|^2}{2m}$

$S = -k_\mathrm{B} \sum_i \mathbb{P}_i \ln \mathbb{P}_i$

$H = -\sum_i \mathbb{P}_i \ln \mathbb{P}_i$

$T^{-1} = \left(\frac{\partial S}{\partial E}\right)_{N,V} \approx \frac{\Delta S}{k_\mathrm{B} \Delta E}$

2 Ensembles

2.1 Microcanonical Ensemble ($\boldsymbol{NVE}$)

$\varphi = \frac{1}{N! h^{3N}} \frac{1}{\Omega} \delta\left[\mathscr{H}(\boldsymbol{q}, \boldsymbol{P}) - E\right]$

$\Omega = \frac{1}{N! h^{3N}} \int \cdots \int \delta\left[\mathscr{H}(\boldsymbol{q}, \boldsymbol{P}) - E\right]\, d^{3N}\boldsymbol{q}\, d^{3N}\boldsymbol{P}$

$\Phi = \frac{1}{N! h^{3N}} \int \cdots \int_{\mathscr{H}(\boldsymbol{q}, \boldsymbol{P}) \le E} d^{3N}\boldsymbol{q}\, d^{3N}\boldsymbol{P} \qquad \Omega = \frac{\partial \Phi}{\partial E}$

$S = k_\mathrm{B} \ln \Omega$

2.1.1 Microcanonical Ideal Gas

$\Omega = \frac{1}{N! h^{3N}} V^N \frac{(2\pi m)^{3N/2}}{\Gamma(3N/2)} E^{3N/2-1}$

$S = N k_\mathrm{B} \left(\ln\left[\frac{V}{N}\left(\frac{4\pi m E}{3Nh^2}\right)^{3/2}\right] + \frac{5}{2}\right)$

$PV = N k_\mathrm{B} T \qquad C_V = \frac{3}{2} N k_\mathrm{B} \qquad C_P = \frac{5}{2} N k_\mathrm{B}$

2.2 Canonical Ensemble ($\boldsymbol{NVT}$)

$\varphi = \frac{1}{N! h^{3N}} \frac{1}{Z} e^{-\beta \mathscr{H}(\boldsymbol{q}, \boldsymbol{P})}$

$Z = \frac{1}{N! h^{3N}} \int \cdots \int e^{-\beta \mathscr{H}(\boldsymbol{q}, \boldsymbol{P})}\, d^{3N}\boldsymbol{q}\, d^{3N}\boldsymbol{P}$

$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$

$S = k_\mathrm{B} \ln Z + \frac{\langle E \rangle}{T}$

$A = -k_\mathrm{B} T \ln Z = U - TS$

2.2.1 Canonical Ideal Gas

$Z = \frac{1}{N! h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{3N/2} V^N$

2.3 Grand Canonical Ensemble ($\boldsymbol{\mu VT}$)

$\varphi = \frac{1}{N! h^{3N}} \frac{1}{\mathcal{Z}} e^{-\beta(\mathscr{H}(\boldsymbol{q}, \boldsymbol{P}, N) - \mu N)}$

$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int \cdots \int e^{-\beta(\mathscr{H}(\boldsymbol{q}, \boldsymbol{P}, N) - \mu N)}\, d^{3N}\boldsymbol{q}\, d^{3N}\boldsymbol{P}$

$\Lambda = -k_\mathrm{B} T \ln \mathcal{Z} = A - \mu N$

2.4 Isothermal–Isobaric Ensemble ($\boldsymbol{NPT}$)

$\varphi = \frac{1}{N! h^{3N}} \frac{1}{z} e^{-\beta(\mathscr{H}_i(\boldsymbol{q}, \boldsymbol{P}) + PV)}$

$z = \frac{1}{N! h^{3N}} \int_0^{\infty} dV \int \cdots \int e^{-\beta(\mathscr{H}(\boldsymbol{q}, \boldsymbol{P}) + PV)}\, d^{3N}\boldsymbol{q}\, d^{3N}\boldsymbol{P}$

$G = -k_\mathrm{B} T \ln z \qquad G = \sum_i \mu_i N_i$

3 Models

3.1 Einstein Solid

$U = \frac{3}{2} N\epsilon + \frac{3N\epsilon}{e^{\epsilon\beta} - 1}$

NVE: $C_V = 3N k_\mathrm{B} (\epsilon\beta)^2 \frac{e^{\epsilon\beta}}{(e^{\epsilon\beta} - 1)^2}$

3.2 Debye Solid

$\omega(k) = 2\sqrt{\frac{\kappa}{m}} \left|\sin \frac{k \delta_\mathrm{lattice}}{2}\right|$

$\omega_\mathrm{D} \equiv \frac{\pi \tilde{c}}{\delta_\mathrm{lattice}} \qquad T_\mathrm{D} \equiv \frac{\hbar \omega_\mathrm{D}}{k_\mathrm{B}}$

$E = \int_0^{\omega_\mathrm{D}} g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\, d\omega \qquad g(\omega) = \frac{3V\omega^2}{2\pi^2 \tilde{c}^3}$

$C_V = 9N k_\mathrm{B} T \left(\frac{T}{T_\mathrm{D}}\right)^3 \int_0^{T_\mathrm{D}/T} \frac{e^x x^4}{(e^x - 1)^2}\, dx \qquad x \equiv \beta\hbar\omega_\mathrm{D}$

3.3 Simplified Ising Model

$\sigma \in \{-1, +1\} \qquad \mathscr{H} = -\sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j$

4 Boson and Fermion Statistics

$\mathcal{Z}_\mathrm{B}^\mathrm{F} = \prod_i \left(1 \pm e^{-\beta(\epsilon_i - \mu)}\right)^{\pm 1}$

$\langle N_i \rangle_\mathrm{B}^\mathrm{F} = (e^{\beta(\epsilon_i - \mu)} \pm 1)^{-1}$ Occupancy function

5 Planck's Law

$B_f = \frac{2hf^3}{c^2} \frac{1}{e^{\beta h f} - 1}$

$u_f = \frac{4\pi}{c} B_f$

6 The Thermodynamic Square

$-S$	$\boxed{U}$	V
$\boxed{H}$		$\boxed{A}$
$-P$	$\boxed{G}$	T

5	$\boxed{1}$	3
2		4

1		4
2		3

$d1 = 2d|3| + 4d|5| \qquad \left(\frac{\partial|1|}{\partial|2|}\right)_3 = \left(\frac{\partial|4|}{\partial|3|}\right)_2$

7 Non-ideal Mixing

$F \in \{H, G, S, V\} \qquad F = \sum_i n_i \bar{F}_i \qquad \bar{F}_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,P,n'}$

$F^\mathrm{E} = F - \sum_i x_i F_i^\circ = \Delta_\mathrm{mix} F - \Delta_\mathrm{mix} F^\circ$

$\Delta_\mathrm{mix} \check{G}^\circ = RT \sum_i x_i \ln x_i \qquad \Delta_\mathrm{mix} \check{G} = RT \sum_i x_i \ln a_i$

$\check{G}^\mathrm{E} = RT \sum_i x_i \ln \gamma_i \qquad \gamma_i \equiv \frac{a_i}{x_i}$

7.1 Binary Solid Solutions

$\Delta_\mathrm{mix} S = k_\mathrm{B} \ln \Omega \qquad \Omega = \frac{(N_1 + N_2)!}{N_1! N_2!}$

$\Delta_\mathrm{mix} S = -k_\mathrm{B}(N_1 + N_2)(x_1 \ln x_1 + x_2 \ln x_2)$

$k_\mathrm{B} = \frac{R}{\mathscr{A}} \qquad N = n\mathscr{A}$

$\check{G}^\circ = x_1 \check{G}_1 + x_2 \check{G}_2 + RT(x_1 \ln x_1 + x_2 \ln x_2)$

8 Phase Transition

Homogeneous nucleation: $\Delta G(r) = \frac{4\pi}{3} r^3 \Delta\check{G} + 4\pi r^2 \gamma \quad R_c = -\frac{2\gamma}{\Delta\check{G}}$

8.1 Mean Field Approximation

$\mathscr{H} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - h \sum_{i=1}^{N} \sigma_i$

$m_i = \langle \sigma_i \rangle \qquad m \in \{-1, 0, +1\} \qquad m = \frac{1}{N} \sum_j m_j = m_i$

$m = \tanh(\beta J m N_\mathrm{neighbours} + \beta h)$ self consistency equation

$T_\mathrm{r} \equiv \frac{T - T_\mathrm{c}}{T_\mathrm{c}} \quad C \propto T_\mathrm{r}^{-\alpha} \quad m \propto -T_\mathrm{r}^{\beta} \quad \alpha, \beta$: critical exponents

$A_\mathrm{MF}(m) = \frac{T}{2} \ln\left(\frac{1 - m^2}{4}\right) - \frac{J N_\mathrm{neighbours}}{2} m^2 + mT \cdot \operatorname{arctanh}(m)$

References

`ISBN-13: 9780199646944,9780444514240`