Miscellaneous

$$f(x,y,z)=0 \qquad \Longrightarrow \qquad \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -1$$

$$k_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T : \text{ Isothermal compressibility}$$

First Law of Thermodynamics

$$dU = d'W + d'Q$$

$$d'Q = dU + PdV \qquad \text{Quasi-static process}$$

Equation of State

$$U = U(T,V)$$

$$C_V \equiv \left(\frac{d'Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad C_p \equiv \left(\frac{d'Q}{dT}\right)_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\beta V$$

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P : \text{ Coefficent of thermal expansion}$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \left(\frac{C_p - C_V}{\beta V} - P\right) dV$$

Clausius inequality (Cycle where heat quantities Q_i are given from sources T_i)

$$\sum_i \frac{Q_i}{T_i} \leqq 0 \qquad \text{(Equal sign denotes reversible process)} \qquad d'Q \leqslant TdS$$

In quasi-static (reversible) process $d'Q = TdS$

$$dU = TdS - PdV = T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right] dV \qquad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

Thermodynamic Functions

Thermodynamic function	Variables	Expression	Minimal change	Euler relation
Internal energy U	S,V	U	$TdS - PdV$	$TS - PV$
Enthalpy H	S,P	$U + PV$	$TdS + VdP$	TS
Helmholtz function F	T,V	$U - TS$	$-SdT - PdV$	$-PV$
Gibbs function G	T,P	$U - TS + PV$	$-SdT + VdP$	0

In case N is considered, μdN is added in minimal change and μN is added in Euler relation

Grand Potential

$$\Omega \equiv F - \mu N \qquad d\Omega = -SdT - PdV - Nd\mu$$

Relational Expression between Thermodynamic Functions

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

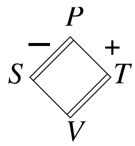
$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left(\frac{\partial\left[\frac{F}{T}\right]}{\partial T}\right)_V$$

Maxwell's Thermodynamic Relations

$$dz = K\,dx + L\,dy \qquad \Longrightarrow \qquad \left(\frac{\partial K}{\partial y}\right)_x = \left(\frac{\partial L}{\partial x}\right)_y$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$



Enegry Equation

$$dS = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV \qquad dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Open System

Chemical potential : $\mu(T, P)$

$$G(T, P, N) = N\mu(T, P)$$

$$dG = -S\,dT + V dP + \mu dN \implies N d\mu + S dT - V dP = 0 \quad \text{(Gibbs-Duhem's equation)}$$

Maxwellian Velocity Distribution

$$N(\boldsymbol{v}) = N\left(\frac{m}{2\pi k T}\right)^{3/2} \exp\left(-\frac{m\boldsymbol{v}^2}{2kT}\right)$$

$$v_{\mathrm{mp}} = \left(\frac{2kT}{m}\right)^{1/2} \qquad \langle v\rangle = \left(\frac{8kT}{\pi m}\right)^{1/2} \qquad \langle v^2\rangle = \frac{3kT}{m}$$

Stirling's Formula

$$n \gg 1 \qquad \Longrightarrow \qquad \begin{array}{ll} n! & \to \sqrt{2\pi n}\, n^n e^{-n} \\ \ln n! & \to n \ln n - n \end{array}$$

Boltzmann's Principle

W : Number of micro-scopic-states in an isolated system

S : Entropy of the system in equilibrium state

$$S = k \ln W$$

Gibbs entropy

$$S = -k \sum_r w_r \ln w_r \qquad w_r \text{ denotes the probability that the state } r \text{ occurs}$$

Distribution of Maxwell-Boltzmann, Fermi-Dirac, and Bose-Einstein

$$\text{Constraints : } \left\{\begin{array}{l} \sum_i N_i = N \\ \sum_i N_i \varepsilon_i = E \end{array}\right. \Longrightarrow \left\{\begin{array}{l} \sum_i \delta N_i = 0 \\ \sum_i \varepsilon_i \delta N_i = 0 \end{array}\right. \qquad \beta \equiv \frac{1}{kT} \qquad \alpha \equiv -\frac{\mu}{kT}$$

i-th cell corresponding to energy ϵ_i is supposed to have G_i states and N_i particles

	How to count number of micro-scopic-states W_D	W_D $\ln W_D$	N_i/G_i
M-B	Distribute N distinguishable particles into $\{N_i\}$ in each i-th cell.	$\frac{N!}{N_1!N_2!\cdots}G_1^{N_1}G_2^{N_2}\cdots$ $N\ln N-\sum_i N_i\ln\frac{N_i}{G_i}$	$e^{-\alpha-\beta\varepsilon_i}$
F-D	Distribute indistinguishable particles into each states w/o overlap. Choose N_i from G_i and arrange the particles by ones into them.	$\prod_i\binom{G_i}{N_i}=\prod_i\frac{G_i!}{N_i!(G_i-N_i)!}$ $\sum_i\{G_i\ln G_i-N_i\ln N_i$ $-(G_i-N_i)\ln(G_i-N_i)\}$	$\frac{1}{e^{\alpha+\beta\varepsilon_i}+1}$
B-E	Distribute indistinguishable particles into each states including overlap. Arrange N_i particles and G_i-1 delimiters in a line divided by rearrangement factors $N_i!$ and $(G_i-1)!$.	$\prod_i\frac{(N_i+G_i-1)!}{N_i!(G_i-1)!}=\prod_i\frac{(N_i+G_i)!}{N_i!G_i!}$ $\sum_i\{-G_i\ln G_i-N_i\ln N_i$ $+(G_i+N_i)\ln(G_i+N_i)\}$	$\frac{1}{e^{\alpha+\beta\varepsilon_i}-1}$

Microcanonical Ensemble

U : Constant

$$Z=\sum_r e^{-\beta\varepsilon_r} \qquad n_r=\frac{N}{Z}e^{-\beta\varepsilon_r}$$

$$U=-N\frac{\partial\ln Z}{\partial\beta} \qquad P=\frac{N}{\beta}\frac{\partial\ln Z}{\partial V}$$

$$S=Nk\ln Z+\frac{U}{T} \qquad \Longrightarrow \qquad F=-NkT\ln Z$$

Canonical Ensemble

N,T,V: Constants

$$w_r=\frac{1}{Z}e^{-E_r/kT} \qquad Z=\sum_r e^{-E_r/kT}$$

w_r : Probability of the energy of the system to be E_r

$$\langle S\rangle=-k\sum_r w_r\ln w_r \qquad S=\frac{U-F}{T}$$

$$\langle U\rangle=-\frac{\partial\ln Z}{\partial\beta}=kT^2\frac{\partial\ln Z}{\partial T} \qquad \langle P\rangle=\frac{1}{\beta}\frac{\partial\ln Z}{\partial V}=kT\frac{\partial\ln Z}{\partial V}$$

$$\langle F\rangle=-kT\ln Z$$

Sum of states of classical statistics

$$Z=\frac{1}{N!}\frac{1}{h^f}\int\cdots\int e^{-\beta H}dq_1\cdots dq_f\,dp_1\cdots dp_f$$

Equipartition Law

If Hamiltonian of a dynamical system is

$$H(q,p)=\sum_{1\le i\le f}a_i p_i^2+\sum_{1\le i,j\le s}b_{ij}q_i q_j \qquad s\le f$$

which gives

$$U=\frac{1}{2}(f+s)NkT$$

Grand Canonical Ensemble

T, V, μ : Constants

Sum of States

$$\Xi(T,\mu)=\sum_{N=0}^{\infty}\lambda^N Z(T,V,N) \qquad \lambda=e^{\beta\mu} : \text{Absolute activity}$$

$$Z(T,V,N)=\sum_r e^{-\beta E_r(N)}$$

$$w_r(N)=\frac{1}{\Xi}e^{-\beta\{E_r(N)-\mu N\}}$$

w_r : Probability that number of particles in the system is N and its energy is $E_r(N)$

$$\langle N\rangle=\lambda\frac{\partial\ln\Xi}{\partial\lambda} \qquad PV=kT\ln\Xi$$

$$P=\left(\frac{\partial[PV]}{\partial V}\right)_{T,\mu} \qquad S=\left(\frac{\partial[PV]}{\partial T}\right)_{V,\mu} \qquad N=\left(\frac{\partial[pV]}{\partial\mu}\right)_{T,V}$$

Grand Sum of States

$$\Xi=\sum_{N=0}^{\infty}\lambda^N\sum_{n_1+n_2+\cdots=N}\exp\left\{-\frac{\sum n_s\varepsilon_s}{kT}\right\}$$

Corrected M-B Distribution

$$\Xi=\sum_{N=0}^{\infty}\frac{\lambda^N z_1^N}{N!}=e^{\lambda z_1} \qquad Z=z_1^N \qquad z_1 : \text{Sum of states in a particle}$$

F-D Distribution

$$\Xi=\prod_s(1+y_s) \qquad y_s=\lambda e^{-\varepsilon_s/kT}$$

B-E Distribution

$$\Xi=\prod_s\frac{1}{1-y_s}$$

Plank's Radiation Formula

Radiance (Energy flow of photons per unit area of the body, solid angle and frequency)

$$I(\nu,\Omega,T)=\frac{2h\nu^3}{c^2}\frac{1}{e^{h\nu/kT}-1}$$

Energy density of photons in the body per frequency

$$u(\nu,T)=\frac{4\pi c^2}{c^3}I(\nu,\Omega,T)=\frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}$$