

Miscellaneous

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

$$1 \text{ cal} = 4.185 \text{ J}$$

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

First Law of Thermodynamics

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

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

Equation of State

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

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

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

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

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

$$\sum_i \frac{Q_i}{T_i} \leq 0 \quad (\text{Equal sign denotes reversible process}) \quad d'Q \leq T dS$$

In quasi-static (reversible) process $d'Q = T dS$

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

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

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

Relational Expression between Thermodynamic Functions

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

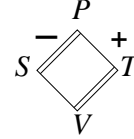
$$S = - \left(\frac{\partial F}{\partial T} \right)_V \quad P = - \left(\frac{\partial F}{\partial V} \right)_T$$

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

Maxwell's Thermodynamic Relations

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

$$\begin{aligned} \left(\frac{\partial T}{\partial V} \right)_S &= - \left(\frac{\partial P}{\partial S} \right)_V & \left(\frac{\partial T}{\partial P} \right)_S &= \left(\frac{\partial V}{\partial S} \right)_P \\ \left(\frac{\partial S}{\partial V} \right)_T &= \left(\frac{\partial P}{\partial T} \right)_V & \left(\frac{\partial S}{\partial P} \right)_T &= - \left(\frac{\partial V}{\partial T} \right)_P \end{aligned}$$



Energy Equation

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_T dV$$

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

Open System

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

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

$$dG = -S dT + V dP + \mu dN \Rightarrow Nd\mu + SdT - VdP = 0 \quad (\text{Gibbs-Duhem's equation})$$

Maxwellian Velocity Distribution

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

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

Stirling's Formula

$$n \gg 1 \quad \Rightarrow \quad \begin{aligned} n! &\rightarrow \sqrt{2\pi n} n^n e^{-n} \\ \ln n! &\rightarrow n \ln n - n \end{aligned}$$

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

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

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

$$\text{Constraints : } \begin{cases} \sum_i N_i = N \\ \sum_i N_i \varepsilon_i = E \end{cases} \Rightarrow \begin{cases} \sum_i \delta N_i = 0 \\ \sum_i \varepsilon_i \delta N_i = 0 \end{cases} \quad \beta \equiv \frac{1}{kT} \quad \alpha \equiv -\frac{\mu}{kT}$$

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 | $\frac{W_D}{\ln W_D}$ | N_i/G_i |
|-----|--|--|--|
| M-B | Distribute N distinguishable particles into $\{N_i\}$ in each i -th cell. | $\frac{N!}{N_1!N_2!\dots} G_1^{N_1} G_2^{N_2} \dots$ $N \ln N - \sum_i N_i \ln \frac{N_i}{G_i}$ | $e^{-\alpha - \beta \varepsilon_i}$ |
| 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

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

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

$$S = N k \ln Z + \frac{U}{T} \quad \Rightarrow \quad F = -N k T \ln Z$$

Canonical Ensemble

N, T, V : Constants

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

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

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

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

$$\langle F \rangle = -k T \ln Z$$

Sum of states of classical statistics

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

Equipartition Law

If Hamiltonian of a dynamical system is

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

which gives

$$U = \frac{1}{2} (f + s) N k T$$

Grand Canonical Ensemble

T, V, μ : Constants

Sum of States

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

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

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

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

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

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

Grand Sum of States

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

Corrected M-B Distribution

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

F-D Distribution

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

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

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