Summary of Thermal laws

- Fundamental Relation $\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V$.
- First Law: $\mathrm{d}E = \delta Q - \delta W$.
- Second Law: $\delta Q = T\delta S$ for quasistatic.

Thermodynamic Potentials

energy $E, \quad E(S,V), \quad \mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V$

enthalpy $H = E + pV, \quad H(S,p), \quad \mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P$

Helmholtz $F = E - TS, \quad F(T,V), \quad \mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$

Gibbs $G = E - TS + pV, \quad G(T,p), \quad \mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$

Maxwell Relations

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

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p, \quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Used to obtain general relation between Spcific heat: let

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{(\partial T)_P}\right); \quad \kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{(\partial P)_T}\right).$$

Recall

$$\delta Q|_x = C_x\,\mathrm{d}T, \quad C_x = T\left(\frac{\partial S}{\partial T}\right)_x$$

and thus $C_p - C_V = VT\alpha^2/\kappa$

- 3rd law : $S \to 0$ as $T \to 0$. Implies

$$C_v \to 0; \quad C_p \to 0; \quad \alpha \to 0; \quad \frac{C_p - C_V}{C_V} \to 0$$

Entropy and Internal Energy : Take (T,V) as indp. var.

- Seek $S(T,V), E(T,V)$.

$$\mathrm{d}S = \frac{C_v}{T}\,\mathrm{d}T + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V,$$

where

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

then

$$C_V(T,V) = C_V(T,V_0) + \int_{V_0}^{V} T\left(\frac{\partial^2 p(T,V')}{\partial T^2}\right)_V \mathrm{d}V'.$$

So

$$S(T,V) - S(T_0,V_0) = \int_{T_0}^{T} \frac{C_v(T',V)}{T'}\,\mathrm{d}T' + \int_{V_0}^{V} \left(\frac{\partial p(T_0,V')}{\partial T}\right)_V \mathrm{d}V'$$

Similarly, for energy:

$$\mathrm{d}E = C_v\,\mathrm{d}T + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\mathrm{d}V$$

and so

$$\frac{\partial E}{(\partial T)_V} = C_v, \quad \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

then, by integration,

$$E(T,V) - E(T_0,V_0) = \int_{T_0}^{T} C_v(T',V)\,\mathrm{d}T' + \int_{V_0}^{V}\left[T_0\left(\frac{\partial p(T_0,V')}{\partial T}\right)_V - p(T_0,V')\right]\mathrm{d}V'$$

Free Expansion: Start from T_1, V_1 and $V_1 \to V_2$:

$\Delta E = Q - W = 0$; for ideal gas: $E(T_1) = E(T_2) \Rightarrow T_1 = T_2$.

In general, temp change:

$$\left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V}\left(p - \frac{T\alpha}{\kappa}\right)$$

$$T_2 = T_1 + \int_{V_1}^{V_2} \mathrm{d}V \left(\frac{\partial T}{\partial V}\right)_E$$

Entropy change:

$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{p}{T} > 0.$$

$$S_2 = S_1 + \int_{V_1}^{V_2} \mathrm{d}V \left(\frac{\partial S}{\partial V}\right)_E$$

- for ideal gas: $\Delta S = N\ln\left(\frac{V_2}{V_1}\right)$
- for van der Waals with Eqn of State $(p + a/v^2)(v - b) = RT$, where $v = V/\nu$ molar vol:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{v-b}; \left(\frac{\partial T}{\partial V}\right)_E = -\frac{a\nu^2}{C_V V^2}$$

and it can be shown:

$$\Delta T = \frac{a\nu^2}{C_V}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

Joule-Thomson Process: start p_1, T_1; $p_1 \to p_2$ and so $T_1 = T_2$

$$\Delta E = -W = p_1V_1 - p_2V_2 \Rightarrow H_1 = H_2$$

- ideal gas:

  $H = E + pV = E(T) + \nu RT \Longrightarrow H(T_1) = H(T_2) \Longrightarrow T_1 = T_2$
- In general:

$$\mu \equiv \left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p}(T\alpha - 1).$$

and also

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p = 0$$

$$\Longrightarrow \left(\frac{\partial S}{\partial p}\right)_H = -\frac{V}{T}$$

$$\Longrightarrow \Delta S = \left(\frac{\partial S}{\partial p}\right)_H \Delta p = -\frac{V}{T}\Delta p$$

Heat Engines and Refrigerators

- heat absorbed by bath: $Q = T\Delta S$.

Heat engine

- Perfect heat engine: convert all heat to work:

$\Delta S_{\text{ttl}} = -q/T = -w/T < 0$.

- Real heat Engine: absorb q_1,emits q_2, produce work $w = q_1 - q_2$: $\Delta S = -q_1/T_1 + q_2/T_2 \geq 0$
- efficiency $\eta \equiv w/q_1 \leq (1 - T_2/T_1)$.
- Carnot Engine: $\Delta S = 0 \Rightarrow \eta_{\max} = (T_1 - T_2)/T_1$

fridge

- Perfect fridge: Does no work in refrigiration $\Delta S = q/_1 - q/T_2$
- real fridge: absorbs q_2 from cold bath, emits q_1 to hot bath, with work $w = q_1 - q_2$.
- coefficient of performance $\eta = q_2/w \leq T_2/(T_1 - T_2)$

Cononical Ensemble: fix T, N, V.

$$P_r = \frac{\exp\left(-\frac{E_r}{T}\right)}{Z}; \quad Z \equiv \sum_r \exp\left(-\frac{E_r}{T}\right)$$

Observables: $\overline{O} = \sum_r \frac{\exp\{-\beta E_r\}}{Z} O_r$

In classical case: $P(E) = \frac{\Omega(E)\exp(-\beta E)}{Z}$

- Maxwell velocity distribution: Consider a classical monatomic gas. Take A = single gas particle and A' remaining molecules, acting as heat resorvoir. at temp. T. Distribution of velocity:

$$f(\vec{v}) = \left(\frac{m}{2\pi T}\right)^{\frac{3}{2}} \exp\left(-\frac{m\vec{v}^2}{2T}\right)$$

- Free energy : $F = -T\ln Z$

Ex: spin in H-field

$E_r = E_\pm = \mp\mu H$

$$P_r = \frac{\exp[\pm\beta\mu H]}{\exp[\beta\mu H] + \exp[-\beta\mu H]} = \frac{\exp[\pm\beta\mu H]}{2\cosh(\beta\mu H)}$$

avg momentun: $\overline{\mu} = \sum_{r=\pm} P_r\mu_r = \mu\tanh(\beta\mu H)$

$\overline{M} = n\overline{\mu} = n\mu\tanh(\mu H/T.)$ when $\mu H \ll T, \overline{M} \approx (n\mu^2 H)/T \equiv \chi H$

Properties of Z, and thermo potential

- avg energy $\overline{E} = -\partial_\beta \ln Z = -T^2\partial_T(F/T)$;
- avg momuntum for spin 1/2: $\overline{\mu} = +T\partial_H \ln Z$
- energy dispersion: $\overline{\Delta E^2} = T^2\partial_T\overline{E} = T^2 C_v$
- $S \equiv -\sum_r P_r \ln P_r = -\partial_T(T\ln Z) = -\partial_T F$;
- $F = E - TS = -T\ln Z = -T\ln\left(\sum_r \exp[-E_r/T]\right)$

Fundamental Relation:

$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$.

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

- Second law for CE: F =min in equil.
- first law in CE: quasistatic change gives $\mathrm{d}\overline{E} = \sum_r E_r\,\mathrm{d}P_r + \sum_r P_r\,\mathrm{d}E_r$
- $\delta Q \equiv \sum_r E_r\,\mathrm{d}P_r = T\,\mathrm{d}S$.
- $\delta W \equiv -\sum_r P_r\,\mathrm{d}E_r$

Grand Canonical Ensemble

- Chemical potential $\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_E = \left(\frac{\partial E}{\partial N}\right)_{S,V}$.
- equilibrium condition: $\mu/T =$ const.
- distribution:

$$P_r = \frac{\exp[-(E_r - \mu N_r)/T]}{\mathcal{Z}}$$

$$\mathcal{Z} = \sum_r \exp[-(E_r - \mu N_r)/T] = \sum_n \exp(\mu N/T) Z(T,N)$$

- particle fluctuation:

$$\overline{E} = \sum_r \frac{\exp[-(E_r - \mu N_r)/T]}{\mathcal{Z}} N_r = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V},$$

where $\Phi = -T\ln Z$, Grand Potential.

Classical Ideal gas

$$Z' = \zeta^N; \quad \zeta = V\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}$$

Correction:

$$Z = Z'/N!$$

$$\Rightarrow F = -NT\ln\left[\frac{eV}{N}\left(\frac{mt}{2\pi\hbar^2}\right)^{3/2}\right]$$

Thermal Classical Limit

$\lambda = \sqrt{(2\pi\hbar^2)/(mT)}$ and then

$$\zeta = \frac{V}{\lambda^3} \Longrightarrow Z = \frac{1}{N!}\zeta\int\prod_{i=1}^{N}\frac{\exp[-\beta U(q)]}{V}d^3\vec{q}$$

Equipartition theroem

Each Quadratic term in Energy $(q \vee p)$ contributes $\frac{1}{2}T$ to the avg energy, and $\frac{1}{2}$ to heat capacity.

- **Ex: harmonic Oscillator**: $E = p^2/2m + \frac{1}{2}kq^2$. Two quad term gives $\overline{E} = 2 * \frac{1}{2}T = T$,

  where kenitic: $\overline{K} = \frac{p^2}{2}m = \frac{\overline{E}}{2}$; potential energy: $\overline{U} = \frac{1}{2}kq^2 = \frac{\overline{E}}{2}$.

  Further, partition function yields:

$$Z = \sum_n e^{-\beta E_n} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

$$\overline{E} = -\partial_\beta \ln(Z) = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{-\beta\hbar\omega} - 1}\right)$$

$$C = \frac{\partial\overline{E}}{\partial T} = \left(\frac{\hbar\omega}{T}\right)^2 \frac{\exp[\hbar\omega/T]}{\exp[\hbar\omega/T] - 1}^2$$

- Thermal limits:

$$T \gg \hbar\omega : \overline{E} \to T; C \to 1.$$

$$T \ll \hbar\omega : \overline{E} \to \hbar\omega/2; C \to \left(\frac{\hbar\omega}{T}\right)^2 \exp[-\hbar\omega/T]$$

Solid Lattice

$$\overline{E} = \sum_{i=1}^{3N}\left(\frac{p_i^2}{2m} + \frac{1}{2}m\omega_i^2 q_i^2\right) = 3NT = 3\nu RT.$$

$$C_v = \left(\frac{\partial\overline{E}}{(\partial T)_V}\right) = 3\nu R.$$

at low temp, assume $\omega_i = \omega =$ const. Let $\theta_E \equiv \hbar\omega$.

$$\overline{E} = 3N\theta_E\left(\frac{1}{2} + \frac{1}{\exp[\beta\theta_E] - 1}\right)$$

$$C_V = \left(\frac{\partial\overline{E}}{(\partial T)_V}\right) = 3N\left(\frac{\theta_E}{T}\right)^2 \frac{\exp[\beta\theta_E]}{(\exp[\beta\theta_E] - 1)^2}$$

Thermal limits:

- $T \gg \theta_E : C_V = 3R$.
- $T \ll \theta_E : C_V = 3R(\theta_E/T)^2 \exp[-\theta_E/T]$

Paramagnetism

- $\vec{\mu} = g\mu_B\vec{v}; \quad \mathcal{E} = -\vec{\mu}\cdot\vec{H} \Longrightarrow \mathcal{E}_m = -g\mu_B H_m$

$$Z = \sum_{m=-J}^{+J}\exp[-\beta g\mathcal{E}_m] = \frac{\sinh\left[(J + \frac{1}{2})\eta\right]}{\sinh(\frac{\eta}{2})},$$

$$\eta \equiv \frac{g\mu_B H}{T}.$$

- avg. momentum:

$$\overline{\mu_z} = \frac{1}{\beta}\frac{\partial\ln Z}{\partial H} = g\mu_\beta J\,B_J(\eta),$$

  where $J\,B_J(\eta) \equiv (J + \frac{1}{2})\coth\left[(J + \frac{1}{2})\eta\right] - \frac{1}{2}\coth(\eta/2))$.
- Magnetization: $\overline{M_z} = n\overline{\mu_z} = ng\mu_B J\,B_J(\eta)$.
  - Thermal limits:

$$\eta \ll 1 : \quad \overline{M_z} = \frac{n(g\mu_B)^2 J(J+1)}{3T}H \equiv \chi H.$$

$$\eta \gg 1 : \overline{M_z} = ng\mu_B J.$$

Kinetic Theory

- maxwell velocity distribution:

$$f(\vec{v}) = \left(\frac{m}{2\pi T}\right)^{3/2}\exp[-(m\vec{v}^2)/(2T)]$$

- distribution for speed $v = |\vec{v}|$:

$$F(v)\,\mathrm{d}v = 4\pi\left(\frac{m}{2\pi T}\right)^{3/2} v^2\exp[-(mv^2)/(2T)]\,\mathrm{d}v$$

  - mean speed: $\overline{v} = \sqrt{8/\pi}\sqrt{T/m}$
  - RMS speed: $v_{\text{RMS}} = \sqrt{3}\sqrt{T/m}$
  - most probable speed: $\tilde{v} = \sqrt{2}\sqrt{T/m}$

Examples:

- Number of particle striking a surface= $n(v_z\,\mathrm{d}t\,\mathrm{d}A), \quad n = N/V$
- total particle flux:

$$\Phi_0 = \int \mathrm{d}^3\vec{v}\Phi(\vec{v}) = \frac{1}{4}n\overline{v}$$

write $\overline{v} = \sqrt{8T/\pi m} \Rightarrow \Phi_0 = \frac{1}{4}n\sqrt{8T/\pi m}$. With $p = nT : \Phi_0 = p/\sqrt{2\pi mT}$ for ideal gas.

- effusion: $I = \Phi_0 * A = pA/\sqrt{2\pi mT}$
- Elastic collision force: $F = mn\overline{v_z^2}\,\mathrm{d}A$.
- $\overline{p} = \frac{F}{\mathrm{d}A} = mn\overline{v_z^2}$
- for ideal gas: $\overline{v_z^2} = T/m \Longrightarrow \overline{p} = nT \Rightarrow pV = NT$