A1 Stat & Thermo

1. Thermodynamics
2. Kinetic Theory
3. Statistical Mechanics

(+ Additions)

1 Thermodynamics

Zeroth Law: System A in thermal equil. with B & System B in equil. with C. $\Leftrightarrow$ A & C in equil.

First Law: $dU = đW + đQ$

exact differential — inexact diff.

$\Rightarrow$ Generally $dU = TdS - pdV$ (Combined with Second Law)

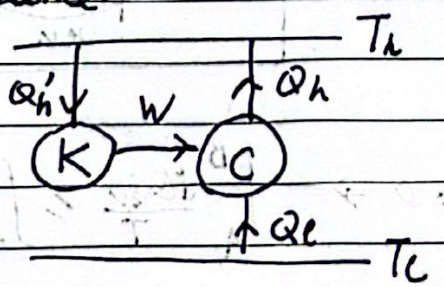
Function of State: any physical quantity with a well-defined value for each equilibrium state of the system. (i.e. U). They must have exact differentials.

Quasi-Static: Slow gradual changes to preserve thermal equilibrium at any time point.

Clausius' Statement of 2nd Law: Impossible to transfer heat from a colder to a hotter body.

Kelvin's Statement: No process is possible whose sole result is the complete transfer of heat into work.

Equivalence:



Carnot engine: most efficient

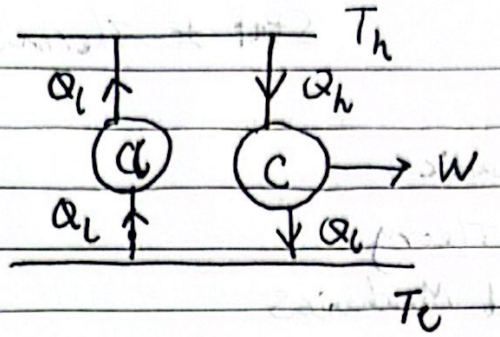
$$\eta = \frac{W}{Q_h} = \frac{Q_h - Q_l}{Q_h}$$

$$\boxed{\eta = 1 - \frac{T_l}{T_h}}$$

$$Q_h/Q_l = T_h/T_l$$

Violate K $\rightarrow$ violate Cl (net transfer of Q_l to T_h)

Similarly

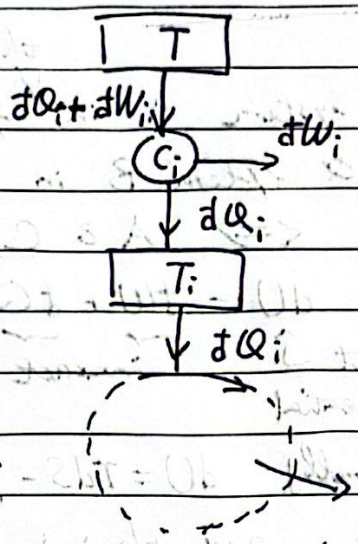


violate Cl → violate K

(net turn of $Q_h - Q_l$ to work)

Carnot Cycle: 2 adiabats + 2 isotherms

Clausius' Theorem



By Carnot engine:

$$\frac{đQ_i + đW_i}{T} = \frac{đQ_i}{T_i}$$

$$đW_i = \left(\frac{T}{T_i} - 1\right) đQ_i \quad \not\rightarrow \quad \Delta W = \sum_i đQ_i = \oint đQ_i$$

$$\Delta W_{tot} = \underbrace{\oint đW_i}_{=\sum_i đW_i} + \underbrace{\oint đQ_i}_{\Delta W} = \oint \frac{T}{T_i} đQ_i = T \oint \frac{đQ_i}{T_i}$$

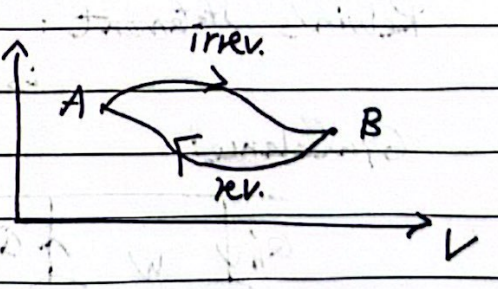
since this violates Kelvin's Statement,

$$\Delta W_{tot} \leq 0 \rightarrow \boxed{\oint \frac{đQ}{T} \leq 0} \quad (T > 0)$$

Clausius Theorem

Entropy

$$dS \equiv \frac{đQ_{rev}}{T}$$



By Clausius' Theorem:

$$\oint \frac{đQ}{T} \leq 0$$

$$\int_A^B \frac{đQ}{T} + \int_B^A \frac{đQ_{rev}}{T} \leq 0 \Rightarrow \int_A^B \frac{đQ_{rev}}{T} \geq \int_A^B \frac{đQ}{T}$$

$$dS = \frac{đQ_{rev}}{T} \geq 0$$

($đQ = 0$ for thermally isolated system)

Treating Universe as thermally isolated $\boxed{dS \geq 0}$ for universe.

Practical Application of Zeroth Law to achieve Thermometers

- Object being measured should have much higher heat capacities than the thermometer material.
- Calibrated column of liquid mercury for temperature scale.
- Measure electrical resistance of a material with well-known dependence on temperature.

Potentials

$$U = U(S, V)$$

$H = U + pV$: Enthalpy $H = H(S, p)$

$F = U - TS$ Free energy $F = F(V, T)$

$G = H - TS$ Free Enthalpy $G = G(T, p)$ (for some potential)

Maxwell's Relations → derive the 2nd cross derivative is very helpful.

Equation of State: Relationship between 2 or more functions of state. (i.e. p, V, T)

Ideal gas

$$pV = nRT = Nk_BT$$

Van der Waals gas $(p + \frac{a}{V^2})(V - b) = RT$

or $p = \frac{RT}{V-b} - \frac{a}{V^2}$ ← intermolecular interactions

↳ finite size of molecules ($V > b$ needed)

Practical Applications

1st Law variants

rod: $dU = TdS + fdL$

liquid surface: $dU = TdS + \gamma dA$

magnetic system: $dU = TdS - mdB$

Curie's law:

$\chi \propto \frac{1}{T}$

$\chi \approx \frac{\mu_0 M}{B}$

Young's modulus: $E_T = \frac{L}{A}\left(\frac{\partial f}{\partial L}\right)_T$ (isothermal)

Linear expansivity: $\alpha_f = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_f$ (can swap L with V, etc.)

try take $d(\lambda U)$ to prove both relations

Euler relation $U = TS - pV + \mu N$

(shown by treating T, p, μ intensive, S, V, N extensive)

Gibbs-Duhem relation $0 = SdT - Vdp + Nd\mu$

Chemical Potential

Consider N to be non-constant

$$dU = TdS - pdV + \mu dN$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{p,T}$$

Euler relation $\Rightarrow$ $U - TS + pV = \boxed{G = \mu N}$

$\mu = \frac{G}{N}$ Gibbs function per particle

If many types of particles: $\mu dN \to \sum_i \mu_i dN_i$

Joule Expansion

(Ideal gas)

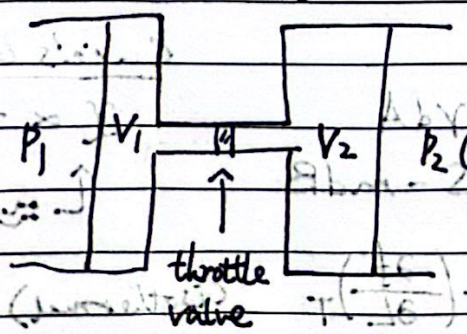
- Irreversible $\rightarrow$ $\Delta S = Nk_B \ln 2 > 0$
- U constant (no work & no heat in)

Joule coefficient: $\mu_J = \left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T$

$$= -\frac{1}{C_V}\Big(\underbrace{T\left(\frac{\partial p}{\partial T}\right)_V}_{\text{depend on eqn. of state.}} - p\Big) \leq 0$$

Joule-Kelvin Expansion

- H is constant



$(\Delta Q = 0)$

$$\Delta U = U_2 - U_1 = p_1V_1 - p_2V_2$$

$$\underbrace{U_1 + p_1V_1}_{H_1} = \underbrace{U_2 + p_2V_2}_{H_2}$$

$$\left(\Delta T = \int_{p_1}^{p_2} \mu_{JK}\, dp\right)$$

Thus J-K coefficient: $\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p \left(\frac{\partial H}{\partial p}\right)_T$

$$= +\frac{1}{C_p}\left(T\left(\frac{\partial V}{\partial T}\right)_p - V\right)$$

μ_{JK} can take either sign.

Critical case when $\mu_{JK} = 0 \rightarrow \underbrace{\left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T}}$

defines inversion curve.

separates cooling & warming.

- Max inversion temperature:

Only below this can J-K expansion result in cooling, which can use for liquefaction of gas.

Microscopic reasons for cooling: Expansion leads to reduced microscopic intermolecular attraction, so potential energy is less negative and increased. This means decreased avg. KE since total U is constant.

Phase Transitions

At constant T, p $\rightarrow dG = 0$ $= -dN_1$ since i indicates phases

$\sum_i \mu_i dN_i = 0 \rightarrow \mu_1 dN_1 + \mu_2 dN_2 = 0$

$\mu_1 = \mu_2$ in phase transitions/equilibrium

Clausius - Clapeyron equation

At phase boundaries: $\mu_1(p,T) = \mu_2(p,T)$

also, $\mu_1(p+dp, T+dT) = \mu_2(p+dp, T+dT)$

Thus to 1st orders, $d\mu_1 = d\mu_2$

(Gibbs-Duhem) $-S_1 dT + V_1 dp = -S_2 dT + V_2 dp$

$$dp/dT = \frac{S_2 - S_1}{V_2 - V_1}$$

$$T\Delta S = \ell \quad \Rightarrow \quad \frac{dp}{dT} = \frac{\ell}{T(V_2 - V_1)} = \frac{L}{T(V_2 - V_1)}$$

P-T gradient of phase boundary

Latent Heat: $L = \Delta Q_{rev} = \underbrace{T_c}_{\text{constant temp.}}(S_2 - S_1)$

Gibbs-phase rule

Various species: $\overbrace{C \text{ components}}^{(C-1) \text{ components because } \sum_{i=1}^{C} x_i = 1}$, each with P diff. phases

Along with p, T as variables.

Phase equilibrium: $\underbrace{\mu_i(P=1) = \mu_i(P=2) = \dots = \mu_i(P=P)}_{(P-1) \text{ eqns}}$

$$\underset{\substack{\uparrow \\ \text{degree of freedoms}}}{F} = \underbrace{2 + P(C-1)}_{\text{variables}} - \underbrace{C(P-1)}_{\substack{\text{constraint} \\ \text{eqns}}} = \boxed{C - P + 2}$$

First-order transitions: discontinuity of 1st-differential of G (i.e. S, V) (plotted against T)

Second-order: discontinuity of 2nd-differential of G (i.e. C_V, C_p)

Third-order: 3rd-differential discontinuity (i.e. $\frac{\partial C_V}{\partial T}$) (i.e. BEC)

...

Continuous phase transitions (do not have associated latent heat)

Dieterici's eqn (for real gas)

$$p(V-b) = RT\exp\left(-\frac{a}{RTV}\right)$$

attractive pressure with Boltzmann factor correction

critical T_c, p_c, V_c found by $\left.\frac{\partial^2 p}{\partial V^2}\right|_T = \left.\frac{\partial p}{\partial V}\right|_T = 0$

② Kinetic Theory

(velocity dist.)

Maxwellian: Boltzmann factor e^{-v^2/v_{th}^2} $\quad v_{th} = \sqrt{\frac{2k_BT}{m}}$

(Assume Isotropic) speed distribution $f(v) \propto v^2 e^{-v^2/v_{th}^2}$

Normalized: $f(v) = \frac{4\pi v^2}{(\sqrt{\pi}\, v_{th})^3} e^{-v^2/v_{th}^2}$

At thermodynamic limit:

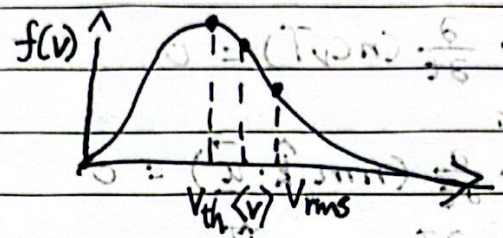
Energy: $U = \frac{1}{2} N m \langle v^2 \rangle$

pressure: $p = mn\langle v_x^2 \rangle = \frac{1}{3} mn \langle v^2 \rangle$

$\langle v \rangle = \frac{2}{\sqrt{\pi}} v_{th}$

$v_{rms} = \sqrt{\frac{3}{2}}\, v_{th}$

$v_{most\ probable} = v_{th}$



$f(v) = 4\pi v^2 g(v_x)$

isotropic speed — velocity in 1 direction

Flux: $d\Phi(\underline{v}) = (n\cos\theta\, v)\, g(\underline{v})\, d^3\underline{v} = n\cos\theta\, v\, g(\underline{v})\, v^2 \sin\theta\, dv\, d\theta\, d\phi$

(hitting wall) $\quad \int d\phi$ integrates to 2π, $2\pi v^2 g(\underline{v}) = \frac{1}{2} f(v)$

$$d\Phi(v) = \Big(\underbrace{\frac{1}{2} n v \cos\theta \sin\theta\, f(v)\, dv\, d\theta}_{\propto (v^3 e^{-v^2/v_{th}^2} \sin\theta\cos\theta)}\Big)$$

no longer isotropic

Effusion

$\Phi = \int d\Phi(v) = \boxed{\frac{1}{4} n \langle v \rangle}$

Assuming $n = \frac{P}{k_BT}$, $\langle v \rangle = \frac{2}{\sqrt{\pi}} \sqrt{\frac{2k_BT}{m}} = \sqrt{\frac{8k_BT}{\pi m}}$

$$\boxed{\Phi = \frac{P}{\sqrt{2\pi m k_BT}}} \rightarrow \frac{dn}{dt} = -\frac{1}{4}\frac{A}{V}\langle v \rangle n$$

Also $\quad \left(\frac{dN}{dt} = -\Phi A\right)$

$\frac{dU}{dt} = -JA$

where $dJ = d\Phi(v)\, \frac{1}{2} m v^2$

Hence $U = U(n, T)$.

Mean collision time

$\tau_c = \frac{1}{n\sigma v}$

Mean free path

$\lambda_{mfp} = \frac{1}{n\sigma}$

Collision cross section: $\sigma = \pi(r_1 + r_2)^2 = \pi d^2$ (if $r_1 = r_2$)

Flux

$$\underbrace{\Pi_z}_{\text{momentum flux}} = -\eta \frac{\partial \langle u_x \rangle}{\partial z} \qquad \underbrace{\eta}_{\text{viscosity}} = \frac{1}{3} n m \lambda \langle v \rangle$$

$$\underbrace{J_z}_{\text{Heat flux}} = -K \frac{\partial T}{\partial z} \qquad \underbrace{K}_{\text{thermal conductivity}} = \frac{1}{3} n c_v \lambda \langle v \rangle$$

$$\underbrace{\mathcal{J}_z}_{\text{Particle flux}} = -D \frac{\partial n^*}{\partial z} \qquad \underbrace{D}_{\text{Self-Diffusion}} = \frac{1}{3} \lambda \langle v \rangle$$

Conservation of (...): $\nabla \cdot \vec{J} + \frac{\partial \rho}{\partial t} = 0$ ($\rho \to$ density; $\vec{J} \to$ flux of ...)

① Heat flux

$$\nabla \cdot \vec{J} + \frac{\partial}{\partial t}(n c_v T) = 0$$

② Momentum flux

$$\nabla \cdot \vec{\Pi} + \frac{\partial}{\partial t}(n m \hat{k} \cdot \vec{u}) = 0$$

$$\Rightarrow \begin{cases} n c_v \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial z^2} & \leftarrow \text{Heat eqn.} \\ n m \frac{\partial \langle u_x \rangle}{\partial t} = \eta \frac{\partial^2 \langle u_x \rangle}{\partial z^2} & \leftarrow \text{Momentum eqn.} \end{cases}$$

Calculations of K, η, D specifically:

η: $$\Pi_z = \int_{v,\theta} \underbrace{\left(\tfrac{1}{2} n v f(v) \cos\theta \sin\theta \, dv \, d\theta\right)}_{d\Phi(v)} \underbrace{\left(-m\lambda \frac{\partial \langle u_x \rangle}{\partial z} \cos\theta\right)}_{\text{Excess momentum}}$$

K: $$J_z = \int_{v,\theta} \left(\tfrac{1}{2} n v f(v) \cos\theta \sin\theta \, dv \, d\theta\right) \underbrace{\left(-c_v \lambda \frac{\partial T}{\partial z} \cos\theta\right)}_{\text{heat deficit/excess}}$$

D: $$\mathcal{J}_z = \int_{v,\theta} \left(\tfrac{1}{2} n v f(v) \cos\theta \sin\theta \, dv \, d\theta\right) \left(-\lambda \frac{\partial n^*}{\partial z} \cos\theta\right)$$

(Assume $\underbrace{L}_{\text{size of container}} \gg \lambda \gg \underbrace{d}_{\text{size of molecule}}$)

Heat sources

$$\nabla \cdot \vec{J} = -\underbrace{c_v}_{\text{per unit volume}} \frac{\partial T}{\partial t} + \underbrace{H}_{\text{Heat generation per unit volume per unit time}}$$

$$\Downarrow$$

$$\boxed{\frac{\partial T}{\partial t} = \frac{K \nabla^2 T}{c_v} + \frac{H}{c_v}}$$

Newton's law of cooling $\quad J = \underbrace{h}_{\text{constant vector}} \Delta T \longrightarrow \Delta T = T - T_{surrounding}$

1-D: thermal diffusion solution $\frac{\partial T}{\partial t} = D\frac{\partial^2 T}{\partial x^2}$

① Separation of variables

② Fourier transforms

General form:

$$T(x,t) = \sum_{\omega} A_{\omega} \exp(-i\omega t)\exp\left((-1+i)\sqrt{\frac{\omega}{2D}}\,x\right)$$

Using sinusoidal initial conditions: i.e. $T(0,t) = T_0 + \Delta T\cos(\Omega t)$

$$\therefore T(x,t) = T_0 + \Delta T\exp\left(-\frac{x}{\delta}\right)\cos\left(\Omega t - \frac{x}{\delta}\right)$$

(take when $\omega = 0, \Omega, -\Omega$ and match the coefficients)

where $\delta = \sqrt{\frac{2D}{\Omega}} = \sqrt{\frac{2K}{\Omega C_V}}$

↳ (skin depth)

Steady state $\frac{\partial T}{\partial t} = 0 \Rightarrow \nabla^2 T = 0$ (Laplace's eqn.)

i.e. Spherically symmetric case: $\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) = 0$

$$T(r) = A + \frac{B}{r}$$ (2 boundary conditions required)

③ Statistical Mechanics

Gibbs entropy

$S_G = \cancel{k_B \ln \Omega} = -k_B \sum_i P_i \ln P_i$

Microcanonical ensemble : collection of systems with identical fixed energy

Canonical ensemble : collection of systems which can exchange energy with a large reservoir.
(T)

Grand Canonical ensemble : Collection of systems which can exchange both energy & particles with a large reservoir.
(T, μ)

Boltzmann factor: $e^{-\beta E}$

Canonical: $P(E) \propto e^{-\beta E}$

Grand canonical: $P(E) \propto e^{-\beta(E-\mu N)}$

Proof:
i.e. Lagrange Multipliers (max S_G subject to constraints of conservation)

Canonical Ensemble

$$Z = \sum_i e^{-\beta E_i} \qquad P_i = \frac{e^{-\beta E_i}}{Z}$$

Quantities:

$$U = -\frac{d \ln Z}{d\beta} \quad (= \sum_i P_i E_i) \quad \text{mean energy}$$

$$F = -k_B T \ln Z$$

$$S = \frac{U-F}{T} = -\left(\frac{\partial F}{\partial T}\right)_V$$

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

$$\boxed{Z = \begin{cases} Z_1^N & \text{disting.} \\ Z_1^N/N! & \text{indisting.} \end{cases}}$$

Applications

spin-half magnet $\qquad E_\pm = \pm \mu B \qquad \mu = \frac{e\hbar}{2m}$ (Bohr magneton)

$$Z_1(\beta) = e^{\beta\mu B} + e^{-\beta\mu B} = 2\cosh(\beta\mu B)$$

SHO $\qquad E_n = \hbar\omega(n + \frac{1}{2})$

$$Z_1(\beta) = \sum_n e^{-\beta\hbar\omega(n+\frac{1}{2})} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

Einstein model of solid: all atoms are independent SHO vibrating with the frq. ω.

$$Z = Z_1^{(3N)}$$

$3N \to N$ particles.

$3 \to$ 3D ; 3 degrees of freedom.

Ideal gas

density of states: $\quad g(k)dk = \frac{V}{(2\pi)^3} 4\pi k^2 dk = \frac{Vk^2}{2\pi^2} dk$

(3D) $\quad \left(\sum_i = \int g(k) dk\right)$

$$Z_1 = \sum_i e^{-\beta E_i} = \int_{k=0}^{\infty} e^{-\beta E(k)} g(k)\, dk \quad \& \text{ Using } Z = \frac{Z_1^N}{N!}$$

(translational modes) Quantum concentration

For $\boxed{E(k) = \frac{\hbar^2 k^2}{2m}}$, $Z_1 = \frac{V}{\lambda_{th}^3}$, $\lambda_{th}^3 = n_Q = \frac{1}{\hbar^3}\left(\frac{m k_B T}{2\pi}\right)^{3/2}$

(non-relativistic) ↳ Thermal wavelength. $\lambda = \hbar\sqrt{\frac{2\pi}{m k_B T}}$

For ultra-relativistic gas: $\boxed{E(k) = \hbar k c}$, $Z_1 = \frac{V}{\Lambda^3}$

$$\Lambda = \frac{\hbar c \pi^{2/3}}{k_B T}$$

	Non-relativistic	relativistic
U	$\frac{3}{2}Nk_BT$	$3Nk_BT$
H	$\frac{5}{2}Nk_BT$	$4Nk_BT$
p	$\frac{2u}{3}$	$\frac{u}{3}$
F	$Nk_BT(\ln(n\lambda_{th}^3)-1)$	$Nk_BT(\ln(n\Lambda^3)-1)$
S	$\underbrace{Nk_B(\frac{5}{2}-\ln(n\lambda_{th}^3))}_{\text{Sackur-Tetrode}}$	$Nk_B(4-\ln(n\Lambda^3))$
Adiabatic Expansion ($dS=0$)	$pV^{5/3} = \text{const.}$	$pV^{4/3} = \text{const.}$

Rotational energy levels: $E_J = \frac{\hbar^2}{2I}J(J+1)$ $\left(= \frac{\hat{J}^2}{2I}\right)$

$$Z_{rot} = \sum_J \underbrace{(2J+1)}_{\text{degeneracy at each level of } J.} e^{-\beta\hbar^2 J(J+1)/2I}$$

Approx. for integration → $Z_{rot} \approx \frac{T}{2\Theta_r}$ $\Theta_r = \frac{\hbar^2}{2Ik_B}$ → rotational temperature ($\sim 10K$)

Vibrational energy levels

1D SHO

$$Z_{vib} = (Z_1)_{SHM} = \frac{e^{-\frac{1}{2}\Theta_v/T}}{1-e^{-\Theta_v/T}} \quad : \Theta_v = \frac{\hbar\omega}{k_B}$$

vibrational temperature ($\sim 3000K$)

Diatomic gas:

C_V: $\frac{3}{2}R \rightarrow \frac{5}{2}R \rightarrow \frac{7}{2}R$

$\sim\Theta_r$ $\sim\Theta_v$

translational	rotational	vibrational
3	2	2

Equipartition Theorem (high T result)

Mean energy $\sim n\frac{1}{2}k_BT$ for n total quadratic modes.

Grand-Canonical Ensemble (N can vary now)

$$\mathcal{Z} = \sum_i e^{\beta(\mu N_i - E_i)} \qquad P_i = \frac{e^{\beta(\mu N_i - E_i)}}{\mathcal{Z}}$$

$$N = \sum_i N_i P_i = k_B T \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_\beta$$

$$U = \sum_i E_i P_i = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_\mu + \mu N$$

$$S = -k_B \sum_i P_i \ln P_i = \frac{U - \mu N + k_B T \ln \mathcal{Z}}{T}$$

Grand potential $\boxed{\Phi_G = -k_B T \ln \mathcal{Z} = F - \mu N}$

Grand differential $d\Phi_G = dF - \mu dN - N d\mu$

$$= -S dT - p dV - N d\mu$$

Also, $\Phi_G = -pV$ (By Euler relation)

No conservation laws $\rightarrow \left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu = 0$ (i.e. photon)

In chemical reactions, G minimized and so:

$$\sum_{j=1}^{p+q} \mu_j dN_j = 0 \longrightarrow \sum_{j=1}^{p+q} \nu_j \mu_j = 0$$

$\mu_j \rightarrow$ chemical potential of j

$\nu_j \rightarrow$ coefficient of j-species

Quantum gas

Bosons: Symmetric wavefunction under particle exchange

$$\psi(\underline{r_2}, \underline{r_1}) = \psi(\underline{r_1}, \underline{r_2})$$

Fermions: Anti-symmetric wavefunction under particle exchange

$$\psi(\underline{r_2}, \underline{r_1}) = -\psi(\underline{r_1}, \underline{r_2})$$

Considering independent particles:

gr. potential: $\mathcal{Z} = \sum_\alpha e^{-\beta(E_\alpha - \mu N_\alpha)}$

Let $\begin{cases} N_\alpha = \sum_i n_i \\ E_\alpha = \sum_i n_i \varepsilon_i \end{cases} \Rightarrow \mathcal{Z} = \sum_{\{n_i\}} \prod_i e^{-\beta(\varepsilon_i - \mu) n_i}$

where n_i is the occupation number (n_i particles at i-th state)

So $\mathcal{Z} = \prod_i \mathcal{Z}_i$ where $\mathcal{Z}_i = \sum_{n_i} e^{-\beta n_i(\varepsilon_i - \mu)}$

$$\begin{cases} \text{Bose gas:} & n_i = 0, 1, 2, \dots \\ \text{Fermi gas:} & n_i = 0, 1 \quad \text{(Pauli-exclusion principle)} \end{cases}$$

$$\mathcal{Z}_i = \left(1 \pm e^{-\beta(\varepsilon_i - \mu)}\right)^{\pm 1} \qquad (\text{'+' for Fermi, '−' for Bose})$$

$$\bar{n}_i = k_B T \frac{\partial \ln \mathcal{Z}_i}{\partial \mu} = \boxed{\frac{1}{e^{\beta(\varepsilon_i - \mu)} \pm 1}}$$

F-D or B-E dist. (mean occupation number of a single-particle state with energy ε_i)

Classical Limit when $\beta(\varepsilon_i - \mu) \gg 1$,

then $\bar{n}_i \to e^{-\beta(\varepsilon_i - \mu)}$ (Boltzmann dist.)

<u>Density of states (again)</u> $g(k)\,dk = \underbrace{(2S+1)}_{\text{degeneracy}} \frac{Vk^2}{2\pi^2} dk$

can obtain $g(E)dE$ either by $\begin{cases} E = \frac{\hbar^2 k^2}{2m} & \text{(quantum)} \\ E = \hbar k c & \text{(ultra-relativistic)} \end{cases}$

$$\sum_i \longrightarrow \int_{E=0}^{\infty} g(E)\,dE$$

so $N = \sum_i \bar{n}_i = \int_0^\infty \frac{g(E)dE}{e^{\beta(E-\mu)} \pm 1}$ $\qquad \Phi_G = -k_B T \sum_i \ln \mathcal{Z}_i$

$U = \sum_i \bar{n}_i E_i = \int_0^\infty \frac{E\, g(E)\,dE}{e^{\beta(E-\mu)} \pm 1}$ $\qquad$ (int. by part.)

$(z = e^{\beta\mu}$, fugacity)

Useful <u>Polylogarithm</u> function $\mathrm{Li}_n(x)$

$$\int_0^\infty \frac{E^{n-1}\,dE}{z^{-1} e^{E} \pm 1} = \Gamma(n)\,\mathrm{Li}_n(\mp z)$$

And $\underset{\substack{\uparrow \\ (\mu=0 \text{ case})}}{\mathrm{Li}_n(1)} = \underbrace{\zeta(n)}_{\text{Riemann zeta}}$

Key result: $\begin{cases} P = \frac{2}{3} u & \text{non-relativistic} \\ P = \frac{1}{3} u & \text{ultra-relativistic} \end{cases}$

Adiabatic change: $\begin{cases} PV^{5/3} = \text{const.} & \text{non-relativistic} \\ PV^{4/3} = \text{const.} & \text{ultrarelativistic} \end{cases}$

Fermi Gas

(exert more pressure than classical)

Fermi energy → energy of the highest occupied state at $T=0$.

$$\varepsilon_F = \mu(T=0)$$

$$\tilde{n}_i(T=0) = \lim_{\beta\to\infty} \frac{1}{e^{\beta(\varepsilon_i-\varepsilon_F)}+1} = \begin{cases} 1 & \varepsilon_i < \varepsilon_F \\ 0 & \varepsilon_i > \varepsilon_F \end{cases}$$

Hence $N = \int_0^{k_F} g(k)\,dk$ $\qquad \varepsilon = \frac{\hbar^2 k^2}{2m}$

$= \int_0^{\varepsilon_F} g'(\varepsilon)\,d\varepsilon$ $\qquad \left(\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}\right)$

$$U = \int_0^{\varepsilon_F} \varepsilon\, g'(\varepsilon)\,d\varepsilon$$

one can show that $\boxed{U = \frac{3}{5} n \varepsilon_F}$

degenerate limit : $T \ll \frac{\varepsilon_F}{k_B} (= T_F)$ (i.e. electrons in metal)

- Qualitative calculation for C_V : (very low T)

$$C_V = \left(\frac{\partial \delta U}{\partial T}\right)_V = \frac{\partial}{\partial T}\Big|_V \left(\Delta N_{excited}\, \Delta\varepsilon\right) \sim \frac{\partial}{\partial T}\Big|_V \left(\left(\underbrace{\frac{N}{\varepsilon_F}}_{g(\varepsilon_F)} \underbrace{k_B T}_{\Delta\varepsilon}\right) k_B T\right)$$

$$C_V \sim \frac{N}{\varepsilon_F} k_B^2 T$$

(factor of $\frac{\pi^2}{2}$ from Sommerfeld expansion)

Application to stars

Fermi momentum $p_F = \hbar k_F = \hbar(3\pi^2 n)^{1/3}$

Elec. deg. pressure → $P_{ele} = \frac{2}{3}u = \frac{2}{3}\left(\frac{3}{5} n \varepsilon_F\right) = \frac{2}{5} n \frac{p_F^2}{2m}$ $(\propto n^{5/3})$

non-relativistic : $P_{ele.}$ can balance $P_{grav.}$ (assume uniform mass dist.)

$\downarrow \propto n^{5/3}$ $\qquad \downarrow \propto n^{4/3}$

But relativistically, $P_{ele} \propto n^{4/3}$ → cannot halt collapse.

Estimating Chandrasekhar limit (white dwarf) $\quad p_F \gtrsim m_e c$

$$n \gtrsim \frac{1}{3\pi^2}\left(\frac{m_e c}{\hbar}\right)^3$$

where $n \approx \frac{Z\rho}{A m_p}$ $\quad (m_e \ll m_p)$

(Neutron star) → change the ratio for $\left(\frac{Z}{A}\right)$ $(0.5 \to 1)$

Bose Gas

(exerts less pressure than classical)

$$n_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1} \qquad (\underline{\mu < \varepsilon_i}, \text{ otherwise } n_i < 0)$$

$\Rightarrow$ $\mu < 0$ generally, take $\mu = 0$ case.

$$\underline{n \le n_Q \zeta\left(\tfrac{3}{2}\right)} \Rightarrow \min T, \max n \text{ for Bose gas} \qquad (n_Q \propto T^{3/2})$$

It is possible for $\frac{n}{n_Q} > \zeta\left(\frac{3}{2}\right)$, however.

For $T \le T_c$ $\rightarrow$ B.E.C. occurs. $\left(T_c = \frac{2\pi\hbar^2}{mk_B}\left(\frac{n}{\zeta(\frac{3}{2})(2s+1)}\right)^{2/3}\right)$

Assume $n(T) \approx n(T_c)$

$$\frac{n_{gnd}(T)}{n(T)} = 1 - \frac{n_{exc.}(T)}{n(T)} \approx 1 - \frac{n_Q(T)}{n_Q(T_c)} \approx \underline{1 - \left(\frac{T}{T_c}\right)^{3/2}}$$

From integrals (polylogarithms) we can get

$$U = \frac{3}{2} N k_B T \frac{Li_{5/2}(z)}{Li_{3/2}(z)}$$

Take $z = 1$ & $T \le T_c$ $\underline{(B.E.C.)}$

$$U_{BEC} = \frac{3}{2} N_{exc.} k_B T \frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} = \frac{3}{2} N k_B T \underbrace{\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}}_{\text{properties of 'excited' particles.}} \left(\frac{T}{T_c}\right)^{3/2}$$

T_c ~ linked to critical temperature of superfluidity.

Photons & Radiation

Radiation pressure: $p = \frac{u}{3}$ (isotropic)

$p = u$ (collimated beam in 1 direction)

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \Rightarrow u = \frac{1}{3}T\left(\frac{\partial u}{\partial T}\right)_V - \frac{u}{3}$$

$$4\frac{dT}{T} = \frac{du}{u} \Rightarrow u = \underbrace{A}_{\text{const.}}T^4$$

Power: $P = \underbrace{\hbar\omega}_{\text{energy of 1 photon}} \underbrace{\Phi}_{\text{flux}} = \frac{1}{4}\underbrace{\hbar\omega n}_{u} c = \underbrace{\left(\frac{1}{4}Ac\right)}_{\sigma} T^4 = \sigma T^4$

↳ (K.T. result) Stefan-Boltzmann

Hence $\begin{cases} u = \frac{4\sigma}{c}T^4 & \text{energy density in radiation} \\ p = \frac{4\sigma}{3c}T^4 & \text{pressure on cavity walls} \end{cases}$

Statistical Mechanics treatment: (photon gas as S.H.O.)

$$g(k)\,dk = \frac{4\pi k^2 dk}{(2\pi/L)^3} \times 2$$

($\omega = ck$) 2 polarizations of EM waves

$$\hookrightarrow g(\omega)\,d\omega = \frac{V\omega^2}{\pi^2 c^3}d\omega$$

density of states

SHO: $U_\omega = -\frac{\partial \ln Z}{\partial \beta} = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1}\right)$

Then $u_{tot} = \frac{1}{V}\int_0^\infty U_\omega\, g(\omega)\,d\omega$

(ignore the $\frac{\hbar\omega}{2}$ contribution which is the contribution of vacuum)

$$\Rightarrow \text{obtain } u = \left(\frac{\pi^2 k_B^4}{15c^3\hbar^3}\right)T^4$$

$$\sigma = \frac{1}{4}Ac = \boxed{\frac{\pi^2 k_B^4}{60c^2\hbar^3}} \quad \text{S-B constant.}$$

Black-body distribution write $U = \int u_\omega\, d\omega = \int u_\nu\, d\nu$
$= \int u_\lambda\, d\lambda$

in ω: $u_\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$

ν: $u_\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\beta h\nu} - 1}$ $\left(\nu = \frac{\omega}{2\pi}\right)$

λ: $u_\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\beta hc/\lambda} - 1}$ $\left(\lambda = \frac{2\pi c}{\omega}\right)$

(Wien's law.)

Differentiate to get max in u_λ or u_ν.

(different, as per unit freq. vs per unit wavelength)