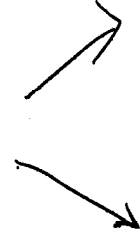


Microscopic



Macroscopic

Statistics



Internal Energy

degrees of freedom
equipartition theorem

1st Law

$$dE = dQ - dW + \mu dN$$

Small systems
large systems

Entropy

- states of a system

$$S \equiv k \ln \Omega$$

$$\Omega \propto E^{3N/2}$$

$$\Delta S \geq 0 \quad \text{2nd Law}$$

$$S \rightarrow 0 \text{ as } T \rightarrow 0 \quad \text{3rd Law}$$

Interactions

Thermal

$$dQ = T ds$$

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E} N, N$$
$$C_V \equiv \left(\frac{\partial Q}{\partial T} \right)_V$$

Heat Transfer

Mechanical

$$dW = F ds$$

$$P \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$
$$K \equiv -V \left(\frac{\partial V}{\partial P} \right)_T$$

isothermal compressibility

Diffusive

$$\Delta S > 0$$

Imposed
Reversible
 $dP=0, dT=0, dQ=0$

Equilibrium

not cold
higher expands
flows to lower potential

Constituents

↳ Ideal gas + non-ideal gas

Maxwell's relations

$$G = \text{Gibbs Free energy}$$

$$= E - TS + PV = \mu N$$

$$F = \text{Helmholtz Free energy}$$

$$= E - TS$$

$$H = \text{Enthalpy} = E + PV$$

Chapter 3: Summary

$$\bar{f} = \sum_s P_s f_s$$

\leftarrow same function
 \uparrow probability

$$\overline{f+g} = \bar{f} + \bar{g}$$

$$\overline{cf} = c\bar{f}$$

$$p+q=1$$

prob that n elements satisfy a criterion + the rest do not.

$$(p+q)^N = \sum_{n=0}^N \frac{N!}{n!(N-n)!} p^n q^{N-n} = 1$$

Prob of being in a given state: $P_N(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}$
 # of diff. configs of N elements for which n satisfy a criterion (Binomial coefficient)
 PN chosen

Stirling's formula: $\ln(m!) \approx m \ln m - m + \frac{1}{2} \ln(2\pi m)$

Trick: $e^x = 10^y \Rightarrow x = \ln 10^y = y \ln 10 \Rightarrow e^x = 10^{x/2.3026}$
 (notes 4-10) [in general: $(b_1)^{x_1} = (b_2)^{x_2} \Rightarrow x_2 = x_1 \ln(b_1) / \ln(b_2)$]

Chapter 4: Large Systems

$$p \equiv \bar{n}/N \quad \leftarrow \text{mean}$$

$$\sigma^2 = \overline{(n-\bar{n})^2} = \sum P_n (n-\bar{n})^2$$

$$\sigma/\bar{n} = \sqrt{q/Np} \quad = Npq = (\text{standard deviation})^2$$

$$P_N(n) \approx \frac{(\bar{n})^n}{n!} e^{-\bar{n}} \leftarrow \text{Poisson (rare successes)}$$

$$P(n) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(n-\bar{n})^2}{2\sigma^2}} \leftarrow \text{Gaussian } (n-\bar{n}) \ll \sigma^2$$

N big only

Random walk; $\overline{(s-\bar{s})^2} = \overline{s^2} - \bar{s}^2 \leftarrow \left[\int_{-\infty}^{\infty} s P(s) ds \right]^2$
 $\equiv (\Delta s)^2 \quad \leftarrow \int_{-\infty}^{\infty} s^2 P(s) ds$

$$\bar{S} = N\bar{s}, \quad \sigma^2 = N(\Delta s)^2$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

Chapter 5 Summary

Internal Energy & Equipartition

I.E. distributed equally among dof if energy in bg^2

$k =$ Boltzmann's const
 $= 1.381 \times 10^{-23} \text{ J/K}$
 $= 0.846 \times 10^{-4} \text{ eV/K}$

$\bar{E} = \frac{1}{2} kT$ per dof

K.E. = $\frac{1}{2} m v^2 = \frac{p^2}{2m} = \frac{(mv)^2}{2m}$

P.E. = $\frac{1}{2} k x^2 = \int_0^x F_{\text{applied}} dx$
 $\uparrow = +kx$

Chapter 6 Summary

Internal Energy & the 1st Law

$kT = 0.025 \text{ eV}$ at $T=300\text{K}$

$dE = dQ - dW + \mu dN \leftarrow$ 1st Law

$W = \int_s \vec{F} \cdot d\vec{s}$
 1 particle \downarrow
 $E = \mu + \underbrace{\frac{1}{2} k r^2}_{\text{potential}} + \underbrace{\frac{1}{2} m v^2}_{\text{kinetic}}$
 (1 dof)
 N particles
 $E = E_{\text{thermal}} + \mu N$

$dE = \text{exact} \leftarrow$ path independent
 $dQ, dW = \text{inexact} \leftarrow$ path dependent

$dF = g dx + h dy$ if $\frac{\partial g}{\partial y} = \frac{\partial h}{\partial x}$
 $\uparrow \frac{\partial F}{\partial x}$ $\uparrow \frac{\partial F}{\partial y}$

Chapter 7 Summary

The States of a System

$P = \frac{1}{\Omega_0} \leftarrow$ states
 prob. $\Omega_0 \leftarrow$ total # dof
 $\Omega_0 = \prod_{i=1}^R \Omega_i$

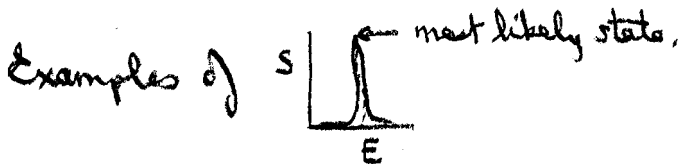
$P_i = \frac{\Omega_i}{\Omega_0} \leftarrow$ subsystem
 $\Omega_0 \leftarrow$ full system

$\int_{E}^{\uparrow} \Omega(E, dE) = g(E) dE$
 $\left. \begin{matrix} \Omega \\ dE \end{matrix} \right\} \leftarrow$ energy spacing = 10^{-24} eV

$\Omega_i(E) \propto E^{\alpha} \leftarrow$ typically $\frac{1}{2} \Rightarrow \Omega_0 \propto E^{R/2}$

Chapter 8 Summary
Entropy + the 2nd Law

$\Delta S_0 \geq 0 \leftarrow$ 2nd Law
 $S = k \ln \Omega \Rightarrow \Delta S \geq 0$
 [J/K]



Chapter 9 Summary
The Thermal Interaction

$S = k \ln \Omega = k R/2 \ln E + \ln(\text{const})$
 $\Omega = \text{const } E^{R/2}$
 Since $\Delta S_0 \geq 0 \Rightarrow \frac{\Delta E_1}{T_1} + \frac{\Delta E_2}{T_2} \geq 0$
 heat flows from hot \rightarrow cold.

$\left. \frac{\partial S}{\partial E} \right)_{V,N} \equiv \frac{1}{T} \rightarrow$ T's equal at \equiv^m
 0th Law

T = measure of how Ω varies with E.
 $\left. \frac{\partial S}{\partial E} \right)_{V,N} = \frac{kR}{2} \cdot \frac{1}{E} \equiv \frac{1}{T}$

$dS = \left. \frac{\partial S}{\partial E} \right)_{V,N} dE$ if V, N const.
 "dQ"
 $\frac{1}{T}$

$\Rightarrow E = \frac{1}{2} k R T = \frac{1}{2} k \nu N T$

$E_{\text{Total}} = \frac{1}{2} k \nu N T + \mu N$

Note, μ may change (define T during phase transition + generate k $\leftarrow E = \frac{1}{2} k T$ (per dof)

$\therefore dQ = T dS$

$\Delta S = k \ln \Omega_2 - k \ln \Omega_1$
 $= k \ln \left(\frac{\Omega_2}{\Omega_1} \right) = \frac{\Delta Q}{T}$

$\therefore \frac{\Omega_2}{\Omega_1} = e^{\Delta Q / kT}$

$S_0 = k \ln \Omega_0 \Rightarrow \Omega = e^{S_0/k}$

$S_0(E) = S_0(\bar{E} + \Delta E) = S_0(\bar{E}) + \left. \frac{\partial S_0}{\partial E} \right)_{V,N} \Delta E + \frac{1}{2} \left. \frac{\partial^2 S_0}{\partial E^2} \right)_{V,N} \Delta E^2$
 $= S_0(\bar{E}) - \frac{Rk}{4\bar{E}^2} \Delta E^2$

$\therefore P(E) = \text{const } \Omega_0(E) = \text{const } e^{S_0(E)/k}$
 $= \frac{1}{\sqrt{2\pi} \sigma} e^{-\Delta E^2 / \sigma^2} \leftarrow$ Gaussian
 $\sigma = \sqrt{\frac{2}{R}} \bar{E} \quad \sigma = R \bar{E}$

$C_V \equiv \left. \frac{\partial Q}{\partial T} \right)_V, C_P \equiv \left. \frac{\partial Q}{\partial T} \right)_P$

$C_V = \left. \frac{\partial Q}{\partial T} \right)_V$
 mass

$C_V = \left. \frac{\partial Q}{\partial T} \right)_V$
 moles

$\Delta Q = \Delta E = \nu N K T$

\Downarrow
 $C_V = \frac{\nu}{2} N k = \frac{\nu}{2} n R$

1 calorie = 4.18 J

molecules/cc
 $= \frac{\rho \cdot A}{M} \frac{\# / \text{gm-mole} \times \frac{1}{2}}{\text{gm/gm-mole}}$
 $\rho = 6.0221367 \times 10^{23}$

Chapter 11 Summary

The Diffusive Interaction

$$\Delta S_0 = \Delta S_1 + \Delta S_2 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Delta E_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) \Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) \Delta N_1 \geq 0$$

$$\therefore \text{at } \Xi^m, T_1 = T_2, P_1 = P_2, \mu_1 = \mu_2.$$

$$\text{approach to } \Xi^m: \Delta S_0 > 0 \Rightarrow \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Delta Q_1 > 0 \Rightarrow \text{hot} \rightarrow \text{cold}$$

$$(P_1 - P_2) \Delta V_1 > 0 \Rightarrow \text{higher } P \text{ expands}$$

$$-(\mu_1 - \mu_2) \Delta N_1 > 0 \Rightarrow \text{flow to lower potential}$$

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V} = k \left(\frac{\partial \ln \Omega}{\partial N}\right)_{E,V} \Rightarrow \frac{\Omega_2}{\Omega_1} = e^{-\mu \Delta N / kT}$$

Chapter 12 Summary

Constraints

$$\Omega_{\text{ideal gas}} \propto E^{3N/2} = \text{const } V^N E^{3N/2} \Rightarrow S_{\text{ideal gas}} = Nk \ln V + \frac{3}{2} Nk \ln E + \text{const.}$$

$$\therefore \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \Rightarrow E = \frac{3}{2} NkT, \quad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T} \Rightarrow \underline{PV = NkT}$$

ideal gas law.

$$Nk = nR$$

$$\therefore PV = nRT$$

$$Pv = RT$$

$$v = \frac{V}{n} = \text{molar vol.}$$

van der Waals eqn of state

$$\left(P + \frac{a}{v^2}\right)(v-b) = RT$$

$$C_v \text{ and } C_p \text{ revisited: } dQ = dE + pdv \quad (N \text{ const})$$

$$= \frac{v}{2} Nk dT + pdv \quad (\mu \text{ const})$$

$$\therefore dq = \frac{v}{2} R dT + pdv \quad (\text{per mole})$$

$$\therefore C_v = \left(\frac{\partial q}{\partial T}\right)_v = \frac{v}{2} R, \quad C_p = \left(\frac{\partial q}{\partial T}\right)_p = \frac{v}{2} R + p \left(\frac{\partial v}{\partial T}\right)_p = C_v + p \left(\frac{\partial v}{\partial T}\right)_p$$

ie $C_p = f_n(v)$ ← link between micro + macro.

" R for ideal gas

since $pv = RT$

$$\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T = -\frac{1}{P}$$

Chapter 13 Summary

Natural Constraints

From perturbation away from Ξ^m , $\Delta S < 0$

$$\Rightarrow \Delta(P/T) \Delta V|_{E,N} < 0 \Rightarrow \uparrow V \uparrow, P/T \downarrow$$

$$\Delta(T \Delta E)|_{V,N} > 0 \Rightarrow \uparrow E \uparrow, T \uparrow$$

$$\Delta(\mu/T) \Delta N|_{E,V} < 0 \Rightarrow \uparrow N \uparrow, \mu/T \downarrow$$

$G =$ Gibbs free energy $\equiv E - TS + pV (= \mu N)$ (t/d potential)

$F =$ Helmholtz free energy $\equiv E - TS$

$H =$ Enthalpy $\equiv E + pV$ ← Heat function
Maxwell's relations

$$dG = -SdT + vdp + \mu dN$$

$$dF = -SdT - pdv + \mu dN \Rightarrow$$

$$dH = Tds + vdp + \mu dN$$

$$\text{had } dE = Tds - pdv + \mu dN$$

$$\left. \begin{aligned} \left. \frac{\partial E}{\partial S} \right|_{V,N} = T, \quad \left. \frac{\partial E}{\partial V} \right|_{S,N} = -P, \quad \left. \frac{\partial E}{\partial N} \right|_{S,V} = \mu \\ \therefore \frac{\partial}{\partial S} \left(\frac{\partial E}{\partial V} \right) = - \frac{\partial P}{\partial S} \Big|_{V,N} = \frac{\partial^2 E}{\partial S \partial V} \\ + \frac{\partial}{\partial V} \left(\frac{\partial E}{\partial S} \right) = \frac{\partial T}{\partial V} \Big|_{S,N} = \frac{\partial^2 E}{\partial V \partial S} \end{aligned} \right\} =$$

$$\therefore - \frac{\partial P}{\partial S} \Big|_{V,N} = \frac{\partial T}{\partial V} \Big|_{S,N}, \text{ etc}$$

48 relations in all.

Measurements: $T + P$, $C_V = \left. \frac{\partial Q}{\partial T} \right|_V = T \left. \frac{\partial S}{\partial T} \right|_V$, $\beta = \left. \frac{1}{V} \frac{\partial V}{\partial T} \right|_P$, $\chi = - \left. \frac{1}{V} \frac{\partial V}{\partial P} \right|_T$
 μ is elusive $\rightarrow \Delta \mu = \frac{\Delta E}{N} - \frac{3}{2} k_B T$ or use electron affinities

Applications of Maxwell's relations:

$$\Delta E = \underbrace{(C_p - PV\beta)}_{\frac{3}{2} k_B T} \Delta T - \underbrace{(T\beta - P\chi)}_{=0} V \Delta P \quad (\Delta N=0) \quad (PV = NRT)$$

$$\text{degree of violation} = \frac{(T\beta - P\chi) V \Delta P}{(C_p - PV\beta) T} \quad \text{True if ideal gas: } \rightarrow \text{for example, } \beta = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P = \frac{NR}{PV}$$

$$\text{Ideal Gas: } C_V = \frac{3}{2} \frac{NR}{n}, C_p = \frac{5}{2} NR$$

$$C \rightarrow 0 \text{ as } T \rightarrow 0$$

Chapter 14 Summary

Imposed Constraints

Possibilities: dN, dV, dQ, dP or dT to 0.

Approach to choice of variables:

1. What property ^{wish} to study?
2. What are the constraints?
3. What can we measure?

Example: Heat water: $dE = \left. \frac{\partial E}{\partial S} \right|_{N,P} \frac{dQ}{T} \Rightarrow dE = \left(T - \left. \frac{\partial V}{\partial S} \right|_{P,N} \right) \frac{dP}{T}$

($dP=0$) isobaric: $dH = Tds$ if $dN=0$ as well \leftarrow heat function

($dT=0$) isothermal: $dF = -pdv$ if $dN=0$ as well \leftarrow work function
 $\chi = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$

($dQ=0$) adiabatic: $dE = -pdv$, $E = \frac{\nu}{2} NKT, PV = NKT \Rightarrow PV^\gamma = \text{const}$
 $\leftarrow ds=0 \text{ at } \equiv^m$ Ideal gas
 $(+ TV^{\gamma-1} = \text{const}) \quad \gamma = \frac{\nu+2}{\nu}$

$$\frac{C_p}{C_v} = \frac{(\frac{\nu}{2}+1)NK}{\frac{\nu}{2}NK} = \frac{\nu+2}{\nu} = \gamma$$

Solids & liq: $ds = \left. \frac{\partial S}{\partial T} \right|_V dT + \left. \frac{\partial S}{\partial V} \right|_T dV = 0 \Rightarrow \frac{dT}{T} = -\frac{\beta}{\chi C_v} dV$

$$= \left. \frac{\partial S}{\partial T} \right|_P dT + \left. \frac{\partial S}{\partial P} \right|_T dP = 0 \Rightarrow \frac{dT}{T} = \frac{V\beta}{C_p} dP \quad \Rightarrow \quad \frac{dV}{V} = -\frac{\chi C_v}{C_p} dP$$

Reversible process: must have $\Delta S=0$ to get back.

Joule Thompson (Throttling) Process

$\Delta Q = 0 = \Delta E + \Delta W$

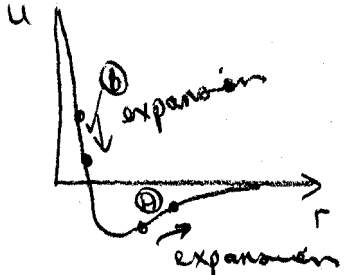
$H = E + PV = \text{const}, \Delta H = 0$

$\Delta S \neq Q\Delta T$ since not \equiv^m
 (used for gas cooling).

$dT = -\frac{V}{C_p} (1 - \beta T) dP$

Free Expansion

$\Delta E = \Delta \left. \frac{E}{V} \right|_0 - \Delta \left. \frac{E}{V} \right|_0 = 0, dE=0 = Tds - pdv \Rightarrow ds = \frac{p}{T} dv$



$dT = \frac{1}{C_v} \left[P - T \left. \frac{\partial P}{\partial T} \right|_V \right] dv = 0$ for ideal gas.

$E = \underbrace{u}_{\text{KE}} + \frac{1}{2} K v^2 + \frac{1}{2} m v^2$

H₂ explosions

Refrigeration

- (A) $u \uparrow$ when $v \uparrow \therefore KE \downarrow \therefore T \downarrow$
- (B) $u \downarrow$ " $v \uparrow \therefore KE \uparrow \therefore T \uparrow$

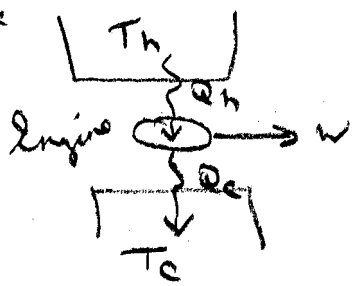
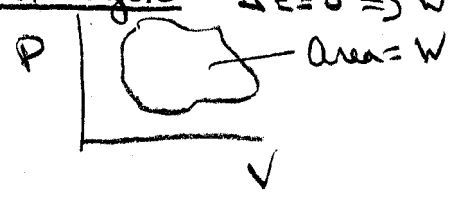
Chapter 15 Summary Engines + Refrigerators

Isothermal: $PV = nRT$, $T = \text{const}$ $\therefore PV = \text{const}$ $\Delta E = \frac{1}{2}kVn\Delta T = 0$

$$\Delta W = \int_{V_i}^{V_f} P dV = nRT \ln(V_f/V_i) = \Delta Q \text{ since } \Delta E = 0$$

Heat Engine

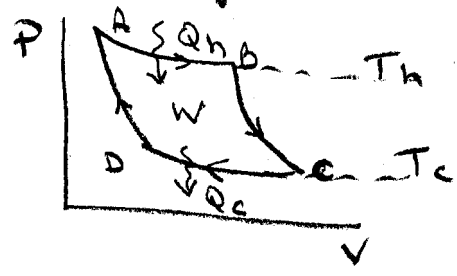
$$\Delta E = 0 \Rightarrow W = Q_h - Q_c$$



$$e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

Heat Pump + refrigerator has arrows reversed

Carnot Cycle



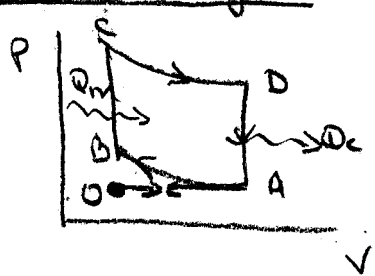
- A \rightarrow B Isothermal expansion
 $Q_h = W_{AB} = nRT_h \ln(V_B/V_A)$
- B \rightarrow C Adiabatic expansion
 $T_h V_B^{\gamma-1} = T_c V_C^{\gamma-1}$
- C \rightarrow D Isothermal compression
 $Q_c = W_{CD} = nRT_c \ln(V_C/V_D)$
- D \rightarrow A Adiabatic compression
 $T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1}$

Can use Carnot cycle to measure temperature.

$$\therefore \frac{V_B}{V_A} = \frac{V_C}{V_D} \Rightarrow \frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

$$\therefore e = 1 - \frac{T_c}{T_h} \text{ for Carnot}$$

Gasoline Engine: Otto cycle



- \rightarrow A intake
- A \rightarrow B Adiabatic Compression, $T \uparrow$
- B \rightarrow C Combustion, Q_h added, $T \uparrow \uparrow$
- C \rightarrow D Power stroke, adiabatic expansion
- D \rightarrow A Exhaust valves open, Q_c removed
- A \rightarrow O Exhaust stroke

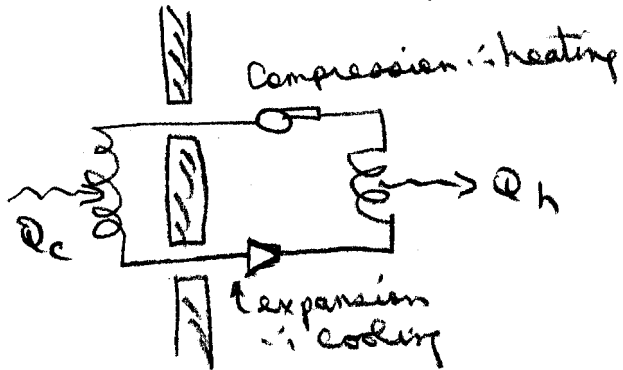
$$e = 1 - \frac{Q_c}{Q_h} = \frac{nC_v(T_c - T_b)}{nC_v(T_d - T_a)}$$

$$= 1 - \frac{(T_D - T_A)}{(T_C - T_B)} \Rightarrow 1 - \frac{1}{(V_1/V_2)^{\gamma-1}}, \quad e \uparrow \text{ as } CR \uparrow$$

\uparrow Compression Ratio
 \leftarrow lower e of Carnot

Chapter 15 Summary (cont'd)

Heat Pumps + Refrigerators



Coeff of Performance \equiv COP
(Heat Pump)

$$= \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c}$$

$$= \frac{T_h}{T_h - T_c} \text{ Carnot}$$

COP (refrigerator)

$$= \frac{Q_c}{W} = \frac{T_c}{T_h - T_c}$$