THERMAL PHYSICS

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Maxwell's Relation

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

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

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

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

> $dU = \cancel{dQ} + dW$
> $= \cancel{dQ} - P\,dV$
> $= T\,dS - P\,dV$

> $H = U + PV$
> $dH = T\,dS + V\,dP$

> $F = U - TS$
> $dF = -P\,dV - S\,dT$

> $G = H - TS$
> $dG = V\,dP - S\,dT$

Phase Transition

$$\frac{dP}{dT} = \frac{\cancel{dQ}}{T\Delta v} = \frac{L}{T(v_g - v_l)}$$

$v_l = \frac{1}{\rho}$ cc/g; $\frac{s_2 - s_1}{v_g - v_l} = \frac{V}{m}$

Thermodynamic Rel^{n}s

* $U = U(T, V)$
  $dU = \cancel{\quad}$

• $C_p = T\left(\frac{\partial S}{\partial T}\right)_P$ • $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$
$dS = \cancel{\quad}$

* $\left(\frac{\partial U}{\partial V}\right)_T = T^2\left[\frac{\partial}{\partial T}\left(\frac{P}{T}\right)\right]_V$

$dU = T\,dS - P\,dV + \mu\,dN$
$dF = \;\; . \;\; + \mu\,dN$
$dG = \;\; . \;\; + \mu\,dN$

* $G(T, P, N) = N f(T, P)$
→ $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = f = \frac{G}{N}$
. $G = \sum \mu_k N_k$ | $G = N\mu$, $dG = \cancel{\quad}$

• $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

• $PV = NK_B T$

$\left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V \cdot \left(\frac{\partial P}{\partial V}\right)_T = -1$

Tds Eqns

$S(T, V)$, $S(T, P)$, $S(P, V)$

Blackbody / EM Wave

$U = bVT^4$, $P = \frac{U}{3V}$

V = const.
$\therefore dS = \frac{dU}{T}$ $S = Vf(T)$
$G = 0 \Rightarrow$ or $\left(\frac{\partial P}{\partial V}\right)_T = 0$

* For ad proces
$-W = dU = C_V\int dT + \int\left(\frac{\partial U}{\partial V}\right)_T dV$

Stat Mech

• Maxwell Boltz. → distinq. / → any.

$\Omega_{MB} = \frac{N!}{\prod_i n_i!}\left[\prod_i g_i^{n_i}\right]$ $n_i \to \epsilon_i$, $d(\epsilon_i) = g_i$

→ $n_i = g_i e^{-\alpha - \beta\epsilon_i}$ (Energy)

$f(\epsilon_i) = \frac{N}{Z} e^{-\beta\epsilon_i} = \left(\frac{n_i}{g_i}\right)$ Distr. Function.

• $Z = \sum_i g(\epsilon_i) e^{-\beta\epsilon_i} \approx \int_0^\infty g(\epsilon) e^{-\beta\epsilon}\,d\epsilon$

• $\ln\Omega = N\ln Z + \beta U$ | $\boxed{\beta = \frac{1}{KT}}$
• $S = K_B \ln\Omega$ | $\left(\frac{\partial S}{\partial U}\right)_V = \cdots$
• $= NK\ln Z + \frac{U}{T}$

• $U = NKT^2\frac{\partial}{\partial T}\ln Z = -N\frac{\partial}{\partial\beta}\ln Z$

• $P(\epsilon) = \frac{e^{-\beta\epsilon}}{Z}$ (Prob of state having ϵ energy)

• $P = -\left(\frac{\partial F}{\partial V}\right)_T$ → Eq^{n} of state
$= NKT\frac{\partial}{\partial V}\ln Z$

• Total No of phase space states $= \int \frac{d^3x\,d^3p}{h^3}$ → Min Vol. $= \frac{4\pi V}{h^3}\int p^2\,dp$

$= \int D(\epsilon)\,d\epsilon$ ideal gas → $\epsilon = \frac{p^2}{2m}$
$D(\epsilon) \equiv g(\epsilon)$ photon → $\epsilon = pc$

Now $Z = $

• $Z_{id} = \frac{V}{h^3}(2\pi mKT)^{3/2}$

• $N(\epsilon)\,d\epsilon = f(\epsilon)\,g(\epsilon)\,d\epsilon$ (No. of particles in energy $\epsilon, \epsilon + d\epsilon$)
$N(v)\,dv$ → $\epsilon = \frac{1}{2}mv^2$

$F(v) = \frac{1}{n}\frac{dn_v}{dv} =$

• $\frac{d}{dv}F(v)\Big|_{v = v_{mp}} = 0$ | $v_{rms} = \sqrt{\frac{\int_0^\infty v^2\,dN(v)}{\int_0^\infty dN(v)}} = \sqrt{\frac{3RT}{M_0}}$

$= \sqrt{\frac{2RT}{M_0}}$

$v_{av} = \frac{1}{\int dN(v)}\int_0^\infty v\,dN(v) = \sqrt{\frac{8}{\pi}\frac{RT}{M_0}}$

• BE → Indist., Any
$f_{BE} = \frac{n}{g} = \frac{1}{e^{\alpha+\beta\epsilon} - 1}$ $\quad {}^{n+r-1}C_{n-1}$

• FD → Indist → only 1
$f_{FD} = \frac{1}{e^{\alpha+\beta\epsilon} + 1}$

photon → $\alpha = 0$
∴ N ↚ not conserved!
$\sum n_i\epsilon_i = E$

Entropical Formulae

$dS_{tot} = dS + dS_R \geq 0$
(sys / Reser./surr)

@ T, V, N → $dF < 0$ | $|W| \leq -\Delta F$
@ P, T, N → $dG < 0$

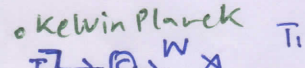
• $\frac{\cancel{dQ}_{rev}}{T} = dS \geq \frac{\cancel{dQ}}{T}$

• $C_V = \left(\frac{\partial U}{\partial T}\right)_V$, $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

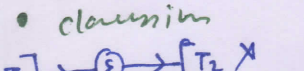
Theorems

• Clausius $\sum_{i=1}^{N}\frac{Q_i}{T_i} \leq 0$

• Kelvin Planck $T_1 > T_2$



• Clausius



• Carnot $\Delta U_{cycle} = W + Q = 0$
$Q = |Q_{in} - Q_{out}|$

$\eta_{cycle} \leq \eta_C = 1 - \frac{T_2}{T_1}$

$\eta = \frac{|W|}{Q_{in}}$

Conversions (CGS) (r-c)

1 cal = 4.184 J
= 4.184 × 10^7 erg

• 1 gm/s^2 = 100 g cm/s^2 → 100 dyne
• 1 N = 10^5 dyne
• 1 atm = 1.0132 bar
1 bar = 10^5 Pa
1 mm Hg = 133.3 Pa
1 erg = 1 dyn-cm
$R = 8.3145\ J = 0.0821\ \frac{L\text{-atm}}{mol\text{-}K} \approx 2\ \frac{cal}{mol\text{-}K}$