Basic concepts

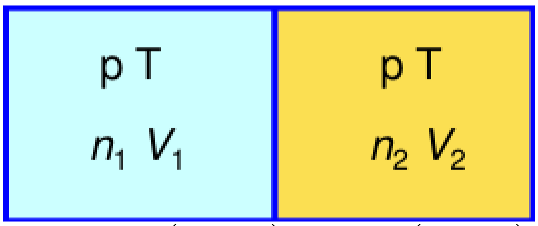
1. Extensive: proportional to N; Intensive: ratio of extensive
2. $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$
3. Carnot's theorem $\dfrac{Q_1}{T_1} = \dfrac{Q_2}{T_2}$
4. Efficiency (for $T_2 > T_1$)
   - $\eta = \dfrac{\text{energy you care about}}{\text{work/heat you used}}$
   - Carnot engine $\eta = \dfrac{\text{work done}}{\text{heat used}} = \dfrac{Q_2 - Q_1}{Q_2}$
   - Refrigerator $\eta = \dfrac{\text{heat removed}}{\text{work done}} = \dfrac{Q_1}{W} = \dfrac{Q_1}{Q_2 - Q_1}$
   - Heat pump $\eta = \dfrac{\text{heat you added}}{\text{work done}} = \dfrac{Q_2}{W} = \dfrac{Q_2}{Q_2 - Q_1} \geq 1$
   - $\eta = 1 - \dfrac{Q_1}{Q_2}$
5. $\mathrm{d}S = \dfrac{\mathrm{d}Q_{rev}}{T} \boxed{\geq \dfrac{\mathrm{d}Q}{T}}$
6. $\boxed{\text{Clausius' theorem } \oint \dfrac{\mathrm{d}Q}{T} \leq 0}$

   where $\mathrm{d}Q$ is heat rejected from engine.

   ($\mathrm{d}Q_{irrev} < \mathrm{d}Q_{rev} < 0$ because friction means more heat released, making $\oint \mathrm{d}Q/T < 0$)
7. $C_V = \left(\dfrac{\mathrm{d}Q}{\mathrm{d}T}\right)_V = T\left(\dfrac{\partial S}{\partial T}\right)_V = \left(\dfrac{\mathrm{d}U}{\mathrm{d}T}\right)_V$
8. $C_p = \left(\dfrac{\mathrm{d}Q}{\mathrm{d}T}\right)_p = T\left(\dfrac{\partial S}{\partial T}\right)_p = \left(\dfrac{\mathrm{d}H}{\mathrm{d}T}\right)_p$
9. Latent heat $L = T(S_2 - S_1)$
10. Ideal gas

$$\begin{aligned} S &= C_V \ln T + nR\ln V + S_0(n) \\ &= nc_V \ln T + nR\ln(V/n) + nS_0', \end{aligned}$$

$$S_0(n) = nS_0' - nR\ln n.$$

11. 

$$\Delta S = n_1 R \ln\left(\frac{V_1 + V_2}{V_1}\right) + n_2 R \ln\left(\frac{V_1 + V_2}{V_2}\right)$$

   - Gibbs' paradox: what if two gases are the same
   - In the above equation, **reversible** isothermal expansion is assumed
   - No process- is reversible for **indistinguishable** particles/gases

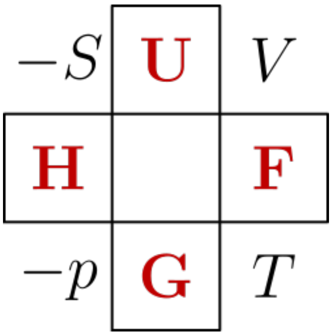
12.

H	Enthalpy	U+pV	**isobaric** heat transfer	
F	Helmholtz free energy	U-TS	**isothermal** work done	
G	Gibbs energy	U+pV-TS	$\boxed{G = \mu N}$	★
Φ_G	Grand potential	$U - TS - \mu N$	$\boxed{\Phi_G = -pV}$	

13. If irreversible (heat flow from resevior to body) and constant p, T,
$-\dfrac{\mathrm{d}G}{T} = -\dfrac{\mathrm{d}U - T\mathrm{d}S}{T} = -\mathrm{d}S_{\text{res}} - \mathrm{d}S_{\text{sys}} = \mathrm{d}S_{\text{total}}$

14. Thermodynamics variables

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$
$$p = -\left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial F}{\partial V}\right)_T$$
$$V = \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T$$
$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_p$$



The thermodynamic square

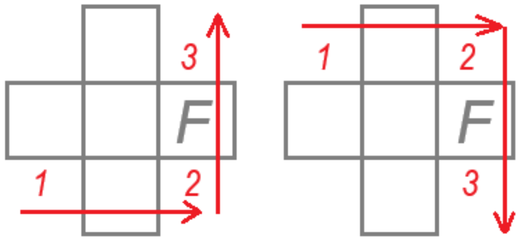
$\boxed{\text{Good Physicist Have Studied Under Very Fine Teachers}}$

Left vars p and S negative sign

$\text{var} = \text{sign}\left(\dfrac{\partial\text{opposite potential}}{\partial\text{opposite var}}\right)_{\text{other var beside potential}}$

Maxwell's relations

- Pick a potential, draw ↱ and ↰ around it
- $\boxed{\left(\dfrac{\partial\, 1}{\partial\, 2}\right)_3}$ (2nd derivative of the potential picked)
- Add sign = sgn(1)sgn(2)sgn(3)



Or use $\boxed{\dfrac{\partial(T,S)}{\partial(p,V)} = 1}$

- $\dfrac{\partial(T,S)}{\partial(x,y)} = \dfrac{\partial(p,V)}{\partial(x,y)}$
- (x,y) can be (T,p), (T,V), (p,S), (S,V)
- $\oint \mathrm{d}U = 0 = \oint T\mathrm{d}S - p\mathrm{d}V$
- $\iint_A \mathrm{d}p\mathrm{d}V = \iint_A \mathrm{d}T\mathrm{d}S$
- Also by Jacobian transformation $\iint_A \mathrm{d}T\mathrm{d}S = \iint_A \dfrac{\partial(T,S)}{\partial(p,V)}\mathrm{d}p\mathrm{d}V$

(better derive it for non-pV systems)

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

15. Partial derivative rules

- $\mathrm{d}f = \left(\dfrac{\partial f}{\partial x}\right)_y + \left(\dfrac{\partial f}{\partial y}\right)_x \mathrm{d}y$
- Maxwell's relations
- $\left(\dfrac{\partial x}{\partial z}\right)_y = 1/\left(\dfrac{\partial z}{\partial x}\right)_y$ ★
- $\left(\dfrac{\partial x}{\partial y}\right)_z\left(\dfrac{\partial y}{\partial z}\right)_x\left(\dfrac{\partial z}{\partial x}\right)_y = -1$

- Measurable quantities $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$, $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$
- Identify a *generalized susceptibility*
  - *isobaric expansivity* $\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$
  - *adiabatic expansivity* $\beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$
  - *isothermal compressibility* $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$
  - *adiabatic compressibility* $\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$ (minus sign to keep it $+ve$)
- Reversible adiabatic expansion $\boxed{pV^\gamma = \text{constant}}$, $\gamma = C_p/C_V = \kappa_T/\kappa_S$

16. Some identities
    - $C_p - C_V = \frac{TV\beta_p^2}{\kappa_T}$
    - isothermal atmosphere $p = p_0 e^{-\frac{m_r gh}{RT}}$
    - constant T, p, $\mathrm{d}S_{\text{total}} = -\frac{\mathrm{d}G}{T}$
    - Gibbs-Helmholtz equation $U = -T^2\left(\frac{\partial F/T}{\partial T}\right)_V$, $H = -T^2\left(\frac{\partial G/T}{\partial T}\right)_p$
    - Joule's expansion (adiabatic/free gas expansion) $\left(\frac{\partial U}{\partial V}\right)_T = 0$ because $U = U(T)$

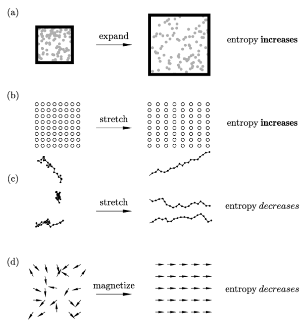
17. Elastic rod
    - $\mathrm{d}U = T\mathrm{d}S + f\mathrm{d}x$
    - Cross sectional area A assumed constant always
    - *Isothermal Young's modulus* $E_T = \frac{\sigma}{\epsilon} = \frac{L}{A}\left(\frac{\partial f}{\partial x}\right)_T$
    - *Linear expansivity at constant tension* $\alpha_f = \frac{1}{L}\left(\frac{\partial x}{\partial T}\right)_f$ (> 0 for wire, < 0 for rubber)
    - $\mathrm{d}F = -S\mathrm{d}T + f\mathrm{d}x$, maxwell: $\left(\frac{\partial S}{\partial x}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_x = AE_T\alpha_f$ $\left(\frac{\partial S}{\partial V}\right)_T = E_T\alpha_f$ (if $\alpha_f > 0$, stretching increases entropy, wire absorbs heat. vice versa for rubber)

18. Surface tension
    - Surface energy $= u(T)\mathrm{d}A$
    - $\mathrm{d}U = T\mathrm{d}S + \gamma\mathrm{d}A$, γ is surface tension (or Helmholtz free energy per unit area at constant T)
    - $u(T) = \left(\frac{\partial U}{\partial A}\right)_T$, $\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_A + \left(\frac{\partial S}{\partial A}\right)_T$, $\mathrm{d}U = T\left(\frac{\partial S}{\partial T}\right)_A \mathrm{d}T + T\left(\frac{\partial S}{\partial A}\right)_T \mathrm{d}A + \gamma\mathrm{d}A = T\left(\frac{\partial S}{\partial T}\right)_A \mathrm{d}T + \left(\gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_A\right)\mathrm{d}A$
      $\boxed{u(T) = \gamma - T\frac{\mathrm{d}\gamma}{\mathrm{d}T}}$ (γ independent of A)
    - Usually $\frac{\mathrm{d}\gamma}{\mathrm{d}T} < 0$, $u(T) > \gamma$
    - Laplace pressure of a bubble $\Delta p = p_{\text{inside}} - p_{\text{outside}} = \frac{2\gamma}{R}$ (Proof)

19. Paramagnetism
    - $\mathrm{d}U = T\mathrm{d}S - m\mathrm{d}B$

- Curie's law $\chi \propto \frac{1}{T}$, $\left(\frac{\partial \chi}{\partial T}\right)_B < 0$
- Assume $\chi \ll 1$, $B = \mu_0(H+M) \approx \mu_0 H$, $\chi = \lim_{H\to 0} \frac{M}{H} \approx \frac{\mu_0 M}{B}$
- Total magnetisation $m = MV$
- Maxwell relation $\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial m}{\partial T}\right)_B \approx \frac{VB}{\mu_0}\left(\frac{\partial \chi}{\partial T}\right)_B$
- Adiabatic temperature change $\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial S}{\partial B}\right)_T \left(\frac{\partial T}{\partial S}\right)_B = -\frac{TVB}{\mu_0 C_B}\left(\frac{\partial \chi}{\partial T}\right)_B > 0$, where $C_B = T\left(\frac{\partial S}{\partial T}\right)_B$ is the heat capacity at constant B
- In labs, material can be cooled to a few millikelvin by adiabatic demagnetization (reduce B)

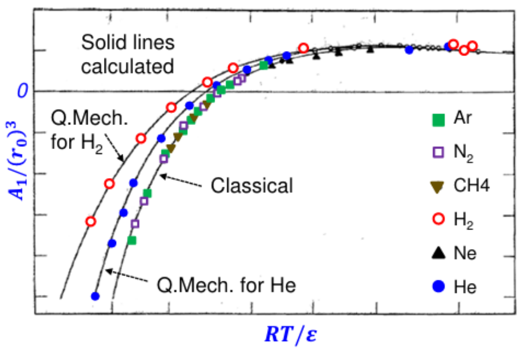
20. Intuition in a picture



Phase transitions

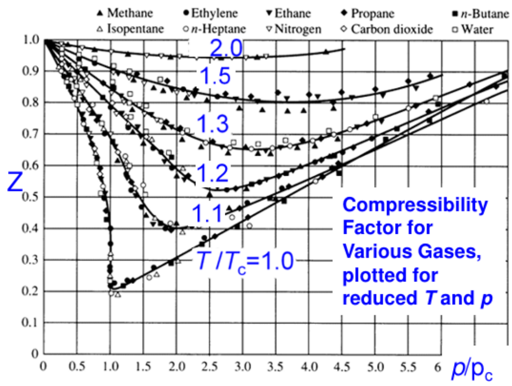
1. EoS of gas

- Boyle's law for ideal gas: $pV = A_0$ where A_0 is a constant. Simple but wrong
- Virial expansion: $pV = A_0 + A_1 p + A_2 p^2 + \cdots = B_0 + B_1/V + B_2/V^2 + \cdots$, $A_i = A_i(T)$
- The *Boyle temperature* T_B is when $A_1(T_B) = 0$
- Gas have similar properties if plotted in reduced variables



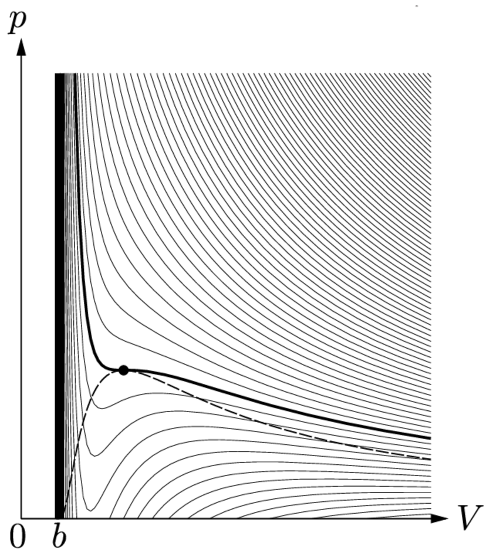
(Noticable deviation for H_2 and He due to quantum effects)

- Real world applications: use measured data of compressibility factor $Z = \frac{pV}{nRT}$

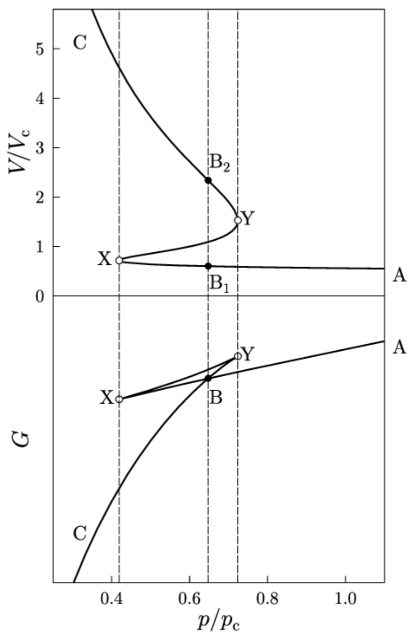


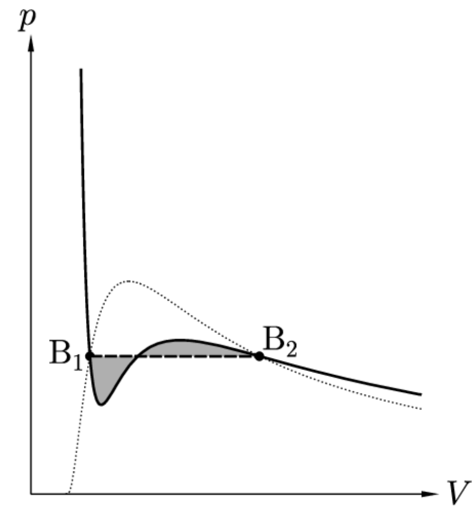
2. Van der Waals' equation

- $\left(p + a\frac{n^2}{V^2}\right)(V - nb) = nRT$ for n moles of gas
- Attraction between molecules reduces potential energy by $a\rho = a\frac{n}{V}$ for each molecule and some a. $U = U_0 - a\frac{n^2}{V}$, $p = \left(\frac{\partial U}{\partial V}\right)_T = p_0 + \frac{an^2}{V^2}$
- Curves at different T. Curve might have negative κ_T, which is unstable. Curve with point of inflexion is the *critical isotherm* with its *critical point*, at *Critical temperature* T_c. (thick line with dot)



  - Critical volume $V_c = 3b$
  - $T_c = 8a/27Rb$
  - $p_c = a/27b^2$
  - $\kappa_T = 1/0$
  - Boyle temperature $T_B = a/Rb$ ($1/V$ expansion)
  - (Hint: $p = \frac{RT}{V-b} - \frac{a}{V^2}$, $\left(\frac{\partial p}{\partial V}\right)_T = 0$, $\left(\frac{\partial^2 p}{\partial V^2}\right)_T$)

- 

  - $p = -\left(\frac{\partial F}{\partial V}\right)_T$
  - $F = f(T) - RT\ln(V-b) - \frac{a}{V}$
  - Constant p and T, minimize $G = F + pV$
  - Equilibrium states minimizes G ($\mathrm{d}G = -T\mathrm{d}S_{total}$, maximizes entropy)
  - Predicts *metastable states* (BXYB) that only happens when not in equilibrium. AB liquid and BC gas *coexist* at B.
  - BY supercooled gas, BX superheated liquid.
- Find point B
  - Same Gibbs energy, $\int_{p_0}^{p_1}\left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p = 0 = \int_{p_0}^{p_1} V\mathrm{d}p$ (The Maxwell construction)
  - 

  - Usually goes straight from B_1 to B_2 at constant p (approximation to a fast process I guess), unless liquid very pure and moves along the curve, then quickly moves across region of negative κ_T to become gas
  - At point B and temperature T_c, the two states are indistinguishable. Also shown by other facts: Densities at T_c become identical, latent heat of vaporisation becomes 0.
- Ways to cool van der Waals gas:
  - Joule expansion (freely expand)
  - Isothermal expansion
  - Joule-Kelvin expansion - high p to low p, constant H. To see dropping pressure causes heating or cooling, the *inversion curve* is defined by $\mu_{JK} = 0 = T\left(\frac{\partial V}{\partial T}\right)_p - V$ or $\left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T}$; $\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T$, $h_i = yh_L + (1-y)h_f$, $y = \frac{h_f - h_i}{h_f - h_L}$, the optimal pressure p_i satisfies $\left(\frac{\partial y}{\partial p_i}\right)_{T_i} = 0$, or $\left(\frac{\partial h_i}{\partial p_i}\right)_{T_i} = -C_p\mu_{JK} = 0$, the best choice is $\mu_{JK} = 0$ on the inversion curve.

3. Gibbs-Duhem equation $N\mathrm{d}\mu = -S\mathrm{d}T + V\mathrm{d}p$★

4. Clausius-Clapeyron equation $\boxed{\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}}$ ★

5. Phase change caveats
   - Liquid/solid to gas $\Delta V = V_{\text{vap}} - V_{\text{liq/solid}} \approx V_{\text{vap}}$
   - Temperature dependence of latent heat usually ignored.
     For ideal gas, $L = L_0 + (C_{p,\text{vapour}} - C_{p,\text{liquid}})T$ ★
   - Solid-liquid boundary, assume $\Delta V \ll 1, L$ independent of T.
     $p = p_0 + \frac{L}{\Delta V}\ln\left(\frac{T}{T_0}\right)$, $\left|\frac{\mathrm{d}p}{\mathrm{d}T}\right| \gg 1$ (very steep)
   - $\Delta V < 0$ from ice to water, $\frac{\mathrm{d}p}{\mathrm{d}T} < 0$

Statistical Intro

1. $\Omega = \Omega(E - E_i)\Omega(E - E_i)$

2. $\beta = \frac{\mathrm{d}\ln\Omega}{\mathrm{d}E}$
   (Condition for $T_1 = T_2$ is $\frac{\mathrm{d}\Omega}{\mathrm{d}E_i} = 0 \implies \frac{\Omega(E_i)'}{\Omega(E_i)} = \frac{\Omega(E-E_i)'}{\Omega(E-E_i)} \implies \frac{\ln\Omega(E_i)}{E_i} = \frac{\ln\Omega(E-E_i)}{E_i}$)

3. Boltzmann distribution $P(E_i) = \frac{e^{-\beta E_i}}{Z}$, partition function $Z = \sum_j e^{-\beta E_j}$, $\beta = \frac{1}{k_B T}$
   ($P(E_i) = \frac{\Omega(E-E_i)}{\Omega(E)}$)

4. Entropy $S = k_B \ln\Omega = \boxed{-k_B \sum_i p_i \ln p_i}$
   (intuition: Time averaged geometric mean/TAGM probability $p_{TAGM} = \sqrt[n]{\prod_i p_i^{np_i}}$, np_i is number of microstates with probablility p_i in time series of length n; Microstates multiply, entropies add, so take log)

5.

	Function of state	Statistical mechanical expression
U		$-\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta}$
F		$-k_\mathrm{B}T\ln Z$
S	$= -\left(\frac{\partial F}{\partial T}\right)_V = \frac{U-F}{T}$	$k_\mathrm{B}\ln Z + k_\mathrm{B}T\left(\frac{\partial \ln Z}{\partial T}\right)_V$
p	$= -\left(\frac{\partial F}{\partial V}\right)_T$	$k_\mathrm{B}T\left(\frac{\partial \ln Z}{\partial V}\right)_T$
H	$= U + pV$	$k_\mathrm{B}T\left[T\left(\frac{\partial \ln Z}{\partial T}\right)_V + V\left(\frac{\partial \ln Z}{\partial V}\right)_T\right]$
G	$= F + pV = H - TS$	$k_\mathrm{B}T\left[-\ln Z + V\left(\frac{\partial \ln Z}{\partial V}\right)_T\right]$
C_V	$= \left(\frac{\partial U}{\partial T}\right)_V$	$k_\mathrm{B}T\left[2\left(\frac{\partial \ln Z}{\partial T}\right)_V + T\left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_V\right]$

   ($U = \langle E\rangle$, $S = -k_B\sum_i P_i \ln P_i = \frac{U}{T} + k_B \ln Z$, $F = U - TS$)

6. If T is not too low (so energy gaps small, summation $\approx$ integral), and T is not too high (modes are quadratic/harmonic)

   - $\langle E\rangle = \int_{-\infty}^{\infty} EP(x)\mathrm{d}x = \dfrac{\int_{-\infty}^{\infty} ax^2 e^{-\beta ax^2}\mathrm{d}x}{\int_{-\infty}^{\infty} e^{-\beta ax^2}\mathrm{d}x} = \dfrac{1}{2\beta} = \dfrac{1}{2}k_BT$ (Feynmann's trick)
   - If $E = \sum_{i=1}^{n} a_i x_i^2$,
   $$\begin{aligned}\langle E\rangle &= \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} EP(x_1,\ldots,x_n)\mathrm{d}x_1\cdots\mathrm{d}x_n\\ &= \sum_{i=1}^{n}\frac{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} a_i x_i^2 e^{-\beta E}\mathrm{d}x_1\cdots\mathrm{d}x_n}{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} e^{-\beta E}\mathrm{d}x_1\cdots\mathrm{d}x_n}\\ &= \sum_{i=1}^{n}\frac{\int_{-\infty}^{\infty} a_i x_i^2 e^{-\beta a_i x_i^2}\mathrm{d}x_i}{\int_{-\infty}^{\infty} e^{-\beta a_i x_i^2}\mathrm{d}x_i} = \sum_{i=1}^{n} a_i\langle x_i^2\rangle = \sum_{i=1}^{n}\frac{k_BT}{2} = \frac{n}{2}k_BT\end{aligned}$$

7. Cool Example: the spin-1/2 paramagnet, Curie's law derived using Z

8. The grand canonical ensemble $P_i = \dfrac{e^{\beta(\mu N_i - E_i)}}{\mathcal{Z}}$, $\mathcal{Z} = \sum_i e^{\beta(\mu N_i - E_i)}$

9. Ensemble: collection of systems/microstates

Name	Microcanonical	Canonical	Grand canonical
Trait	Vanilla one	heat reservoir	heat & particle reservoir
Key function	$\Omega = e^{\beta TS}$	$Z = e^{-\beta F}$	$\mathcal{Z} = e^{-\beta\Phi_G}$

10. The Third law: $\boxed{\lim_{T\to 0} S = 0}$ (for crystal/system in equilibrium. Counter-example: glass, not in equilibrium, not perfect crystal)

11. Consequences at $T\to 0$ due to 3rd law

   - Heat capacity goes to 0 because $C = T\dfrac{\partial S}{\partial T} = \dfrac{\partial S}{\partial \ln T}$, $\ln T\to -\infty$, $S\to 0$
   - Thermal expansion stops $\left(\dfrac{\partial S}{\partial p}\right)_T = \left(\dfrac{\partial V}{\partial T}\right)_p$, $\beta_p = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_p$
   - Gas not ideal $C_p - C_v \to 0 \neq R$, $S = C_V\ln T + R\ln V + \cdots \to -\infty$ is wrong
   - Curie's law breaks down $\left(\dfrac{\partial S}{\partial B}\right)_T = \left(\dfrac{\partial m}{\partial T}\right)_B = \dfrac{VB}{\mu_0}\left(\dfrac{\partial \chi}{\partial T}\right)_B \to 0$, $\chi \propto 1/T$ fails (magnetic moments' interactions dominant, which was ignored at high T)
   - Unattainability of absolute 0 in finite number of steps (Well, experimentally...)
   - Two phases have 0 latent heat if they coexist at $T = 0$. $\dfrac{\mathrm{d}p}{\mathrm{d}T} = \dfrac{\Delta S}{\Delta V} \to 0$ (tested for ^{4}He and ^{3}He)

Photons

1.

Name	Symbol	Experssion
spectral energy density	$u_\lambda(\lambda, T)$	$u(T) = \int u_\lambda \mathrm{d}\lambda$
flux of photons	Φ	$\int nc\cos\theta \frac{\mathrm{d}\Omega}{4\pi} = \frac{1}{4}nc$
flux of energy	energy incident per area per time	$\int \frac{1}{4}n_\epsilon(\epsilon)\epsilon c\mathrm{d}\epsilon = \int \frac{1}{4}u_\epsilon(\epsilon)c\mathrm{d}\epsilon = \int \frac{1}{4}u_\lambda(\lambda)c\mathrm{d}\lambda$
spectral absorptivity	$\alpha_\lambda(\lambda)$	energy absorbed = $\alpha_\lambda \times$flux of energy
spectral radiant exitance	energy emitted per area per wavelength	$e_\lambda(\lambda, T)$

2. $\boxed{u = \left(\frac{\partial U}{\partial V}\right)_T = \int_0^\infty \epsilon n(\epsilon)\mathrm{d}\epsilon}$
3. Blackbody: absorb anything $\alpha_\lambda = 1$
4. Number of photons hitting surface per unit time $\int_{\theta=0}^{\pi/2} n(c\cos\theta)\frac{\mathrm{d}\Omega}{4\pi}$, where $\frac{\mathrm{d}\Omega}{4\pi} = \frac{1}{2}\sin\theta\mathrm{d}\theta$
5. Radiation pressure $p = \frac{u}{3} = \int_{\epsilon=0}^{\infty}\int_{\theta=0}^{\pi/2}\left(\frac{2\epsilon\cos\theta}{c}\right)n_\epsilon\mathrm{d}\epsilon(c\cos\theta)\frac{1}{2}\sin\theta\mathrm{d}\theta$
6. Kirchhoff's law $e_\lambda\mathrm{d}\lambda = \alpha_\lambda\left(\frac{1}{4}u_\lambda c\mathrm{d}\lambda\right)$, $\boxed{\frac{e_\lambda}{\alpha_\lambda} = \frac{1}{4}u_\lambda(\lambda, T)c}$
7. Stefan-Boltzmann law
   - $U = u(T)V$, $u = \left(\frac{\partial U}{\partial V}\right)_T$
   - $u = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p$
   - $p = u/3$
   - $u = \frac{1}{3}\left(T\frac{\mathrm{d}u}{\mathrm{d}T} - u\right)$, $u = CT^4$
   - Power emitted per unit are per unit time
     $P = \int e_\lambda\mathrm{d}\lambda = \int \frac{1}{4}u_\lambda c\mathrm{d}\lambda = \frac{1}{4}uc = \frac{1}{4}cCT^4 = \sigma T^4$
   - $\sigma = \frac{\pi^2 k_B^4}{60\hbar^3c^2} = 5.67\times10^{-8}\mathrm{Wm^2K^{-4}}$
8. $\mu = 0$ for photon
   - $G = U + pV + TS$, $g = u + p + Ts$
   - $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$, if $\mathrm{d}V = 0$, $\mathrm{d}u = T\mathrm{d}s = \mathrm{d}q$
   - $\mathrm{d}q = \mathrm{d}u = 4CT^3\mathrm{d}T$
   - $s = \int_0^T \frac{\mathrm{d}q}{T} = \int_0^T 4CT^2\mathrm{d}T = \frac{4}{3}CT^3 = \frac{4}{3}u$
   - $\mu = g = u + \frac{u}{3} - \frac{4}{3}u = 0$
   - Photons can be created or destroyed, $\mathrm{d}N_{\text{total}} \neq 0$ works
9. Bose integral $\int_0^\infty \frac{x^n}{e^x - 1}\mathrm{d}x = \zeta(n+1)\Gamma(n+1)$ ★

   Thus, $\int_0^\infty \frac{x^n e^x}{(e^x-1)^2}\mathrm{d}x = n\zeta(n)\Gamma(n)$ by Feymann's trick

10. Stefan-Boltzmann factor

- $E_n = n\hbar\omega$ (ground state energy $\dfrac{\hbar\omega}{2}$ subtracted for a finite summation)
- $Z = \displaystyle\sum_{n=0}^{\infty} e^{-\beta E_n} = \frac{1}{1-e^{-\beta\hbar\omega}}$
- $U = -\dfrac{\mathrm{d}\ln Z}{\mathrm{d}\beta} = \dfrac{1}{Z}\dfrac{\hbar\omega e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2} = \dfrac{\hbar\omega}{e^{\beta\hbar\omega}-1}$
- k-space, 2 polarisations, positive k/one octant, $\dfrac{pi^3}{L^3}$ each mode, $g(k)\mathrm{d}k = 2\left(\dfrac{4\pi k^2\mathrm{d}k}{8}\right)/\dfrac{\pi^3}{L^3}$, $g(k) = \dfrac{Vk^2}{\pi^2}$
- $\omega/k = c$
- $g(\omega) = g(k)\dfrac{\mathrm{d}k}{\mathrm{d}\omega} = \dfrac{Vk^2}{c\pi^2} = \dfrac{V\omega^2}{c^3\pi^2}$
- $u(\omega, T) = g(\omega)u = \dfrac{g}{V}U = \boxed{\dfrac{\omega^2}{c^3\pi^2}\dfrac{\hbar\omega}{e^{\beta\hbar\omega}-1}}$
- $u(T) = \dfrac{\hbar}{\pi^2c^3}\displaystyle\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega^3}-1}\mathrm{d}\omega = \frac{\hbar}{\pi^2c^3}\left(\frac{1}{\hbar\beta}\right)^4\int_0^\infty \frac{x^3\mathrm{d}x}{e^x-1}$
- $\displaystyle\int_0^\infty \frac{x^3\mathrm{d}x}{e^x-1} = \zeta(4)\Gamma(4) = \frac{\pi^4}{90}\cdot 6 = \pi^4/15$
- $u(T) = \dfrac{k^4\pi^2}{15\hbar^3c^3}T^4 = \dfrac{4\sigma}{c}T^4$
- $\omega = \dfrac{2\pi c}{\lambda}$,$u(\lambda, T) = u(\omega, T)\left|\dfrac{\mathrm{d}\omega}{\mathrm{d}\lambda}\right| = \dfrac{8\pi ch}{\lambda^5(e^{hc/\lambda kT}-1)}$ ($|\cdot|$ sign works limits of integration also changed)
- Wien's displacement law $\dfrac{\mathrm{d}u(\lambda, T)}{\mathrm{d}\lambda} = 0$

11. 1D *velocity* distribution

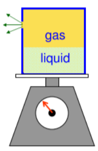
- $f_{1D} \propto e^{-\beta E}$
- $f_{1D}(v) = \sqrt{\dfrac{m}{2\pi kT}}e^{-mv^2/2kT}$
- $\displaystyle\int_{-\infty}^{\infty} f_{1D}(v)\mathrm{d}v = 1$
- $\langle|v|\rangle = \sqrt{\dfrac{2kT}{\pi m}}$
- $\langle v^2\rangle = \dfrac{kT}{m}$
- Equipartition: $\langle KE\rangle = \dfrac{1}{2}m\langle v^2\rangle = \dfrac{1}{2}kT$

12. 3D *speed* distribution

- $f_{3D}\mathrm{d}v \propto (f_{1D}\mathrm{d}v_x)^3 = (f_{1D})^3v^2\mathrm{d}v$ (v^2 from spherical coordinates' Jacobian)
- $\displaystyle\int_0^\infty f_{3D}(v)\mathrm{d}v = 1$
- Maxwell-Boltzmann: $f(v) = \dfrac{4}{\sqrt{\pi}}\left(\dfrac{m}{2kT}\right)^{3/2}v^2e^{-mv^2/2k_BT}$
- $\langle v\rangle = \sqrt{\dfrac{8kT}{\pi m}}$
- $\langle v^2\rangle = \dfrac{3kT}{m}$, $v_{rms} = \sqrt{\dfrac{3kT}{m}}$ (satisfies equipartition)

- Most probable $v_{f_{max}} = \sqrt{\dfrac{2kT}{m}}$
- $v_{f_{max}} < \langle v \rangle < v_{rms}$, $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$
- Collision rate $= \dfrac{1}{2} A v_x N/V$
- Average pressure on wall $= p = m v_x^2 \dfrac{N}{V} = \dfrac{1}{3} m \langle v^2 \rangle \dfrac{N}{V}$
- $pV = \dfrac{1}{3} N m \langle v^2 \rangle = nRT$, $U = \dfrac{1}{2} N m \langle v^2 \rangle = \dfrac{3}{2} nRT$
- n of particles with speed $\in [v, v + \mathrm{d}v]$ and angle $\in [\theta, \theta + \mathrm{d}\theta]$ is $\boxed{n f(v) \mathrm{d}v \dfrac{1}{2} \sin\theta \mathrm{d}\theta}$
- More rigourour way: $p = \displaystyle\int_0^\infty \int_0^{\pi/2} (2mv\cos\theta) \left(v\cos\theta \; n f \mathrm{d}v \; \frac{1}{2} \sin\theta \mathrm{d}\theta \right) = \frac{1}{3} mn \langle v^2 \rangle$
- Dalton's law: $p = \left(\displaystyle\sum_i n_i \right) kT = \sum_i p_i$ (p is mass-independent)

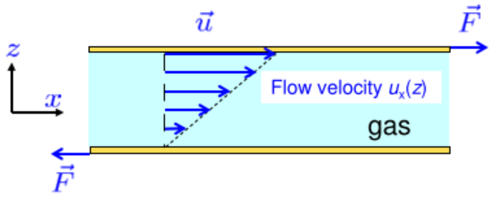
13. Effusion: particle passes through a tiny hole without colliding
14. Flux (of anything) $= \Phi = \dfrac{\text{num particles/quantity you care about}}{\text{area} \times \text{time}}$
15. Effusion rate $= \Phi A$
16. $\mathrm{d}N = nv\cos\theta f(v) \mathrm{d}v \dfrac{1}{2} \sin\theta \mathrm{d}\theta \propto v f(v) \propto v^3 e^{-mv^2/2kT}$
17. $\boxed{\Phi = \dfrac{1}{4} n \langle v \rangle} = \dfrac{p}{\sqrt{2\pi mkT}}$. Graham's law: $\Phi \propto \dfrac{1}{\sqrt{m}}$ at constant pressure
18. Knudsen method for vapour pressure measurment $p = \sqrt{\dfrac{2\pi kT}{m}} \dfrac{1}{A} \left(\dfrac{\mathrm{d}M}{\mathrm{d}t} \right)$, $\dfrac{\mathrm{d}M}{\mathrm{d}t} = -m\Phi A$ is rate of mass loss

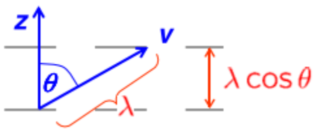


19. Collision cross section $\sigma = \pi(r_1 + r_2)^2$. For identical particles, $\boxed{\sigma = \pi(2r)^2} = \pi d^2$
20. Mean free path
    - Chance of collision $n\sigma v \delta t$, where σ is collision cross-section
    - Chance of no collision from t to $t + \delta t$ related by $P(t + \delta t) = P(t)(1 - n\sigma v \delta t)$
    - $P(t + \delta t) \approx P(t) + \dfrac{\mathrm{d}P}{\mathrm{d}t} \delta t$, $\dfrac{1}{P} \dfrac{\mathrm{d}P}{\mathrm{d}t} = -nv\sigma$, $P(0) = 1$, $\boxed{P(t) = e^{-nv\sigma t}}$
    - Probability of colliding first time between $[t, t + \mathrm{d}t]$ is $e^{-nv\sigma t} n\sigma v \mathrm{d}t$, mean collision/scattering time $\boxed{\tau = \dfrac{1}{n\sigma v}} = \displaystyle\int_0^\infty t e^{-n\sigma t} n\sigma v \mathrm{d}t$
    - $\lambda \approx \langle v \rangle \tau \approx \dfrac{\langle v \rangle}{n\sigma \langle v_r \rangle}$
    - Mean relative velocity $\langle v_r \rangle = \langle |\mathbf{v}_1 - \mathbf{v}_2| \rangle = \langle \sqrt{v_1^2 + v_2^2 - 2\mathbf{v}_1 \cdot \mathbf{v}_2} \rangle$
      $\approx \sqrt{\langle v_1^2 \rangle + \langle v_2^2 \rangle - 2|v_1||v_2| \underbrace{\cancel{\langle \cos\theta \rangle}}_{=0}} \approx \sqrt{\langle v_1 \rangle^2 + \langle v_2 \rangle^2} = \sqrt{2} \langle v \rangle$
    - $\boxed{\lambda = \dfrac{1}{\sqrt{2} n\sigma} = \dfrac{kT}{\sqrt{2} p\sigma}}$

21. Viscosity

- Moment flux $\Pi_z = -\tau_{xz} = -\eta \frac{\mathrm{d}\langle v_x \rangle}{\mathrm{d}z}$ (transfer momentum between top/bottom plates)

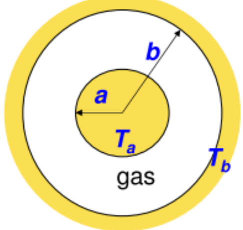




- Momentum transported to plates in x direction $-m\frac{\mathrm{d}\langle v_x \rangle}{\mathrm{d}z}\lambda\cos\theta$
- $\tau_{xz} = -\Pi_z = \frac{1}{3}nm\lambda\langle v \rangle \frac{\partial \langle v_x \rangle}{\partial z} = \eta \frac{\partial \langle v_x \rangle}{\partial z}$
- Dynamic velocity $\boxed{\eta = \frac{1}{3}nm\lambda\langle v \rangle}$
  - independent of pressure (or n because $p = nkT$)
    $\eta = \frac{1}{3}nm\langle v \rangle \frac{1}{\sqrt{2}n\sigma} = \frac{m\lambda\langle v \rangle}{3\sqrt{2}\sigma}$
  - Kinematic viscosity $\nu = \eta/\rho$ (diffusivity of momentum)
  - For *gas*, $\eta = \frac{2}{3\pi d^2}\sqrt{mkT} \propto \sqrt{T}$, $\eta \propto \sqrt{m}$
  - $L \gg \lambda \gg d$, L is container size, d is molecule diameter
  - Liquid $\lambda \sim d$, $\eta \propto e^{1/T}$ (Arrhenius equation)
  - σ decreases are T increases, ignored
  - Maxwell distribution not suitable having a range of different v. Chapman & Enskog replaced $\frac{2}{3\pi}$ in η to $\frac{5}{16}$

22. Thermal conductivity

- $\mathbf{J} = -\kappa \boldsymbol{\nabla} \mathbf{T}$
- $\boxed{\kappa = \frac{1}{3}C_V\lambda\langle v \rangle}$, where $\boxed{C_V = nC_{\text{molecule}}}$ is heat capacity per unit volume
- $\boxed{\kappa = C_{v,s}\eta}$, where $C_{v,s} = \frac{C_{\text{molecule}}}{m}$ is specific heat capacity
- Each molecule assumed to transfer same amount of heat. Improve by considering it $\propto$ translational KE, $\kappa = (C_{trans} + C_{rot})\eta = (\frac{5}{2}C'_{v,s} + C''_{v,s})$
- Eucken's formula $\kappa = \frac{1}{4}(9\gamma - 5)\eta C_{v,s}$
- Measure κ by heating cylinder center



$Q = 2\pi r J = 2\pi r(-\kappa\frac{\partial T}{\partial r})$, $\boxed{\kappa = \frac{Q}{2\pi}\frac{\ln(b/a)}{T_a - T_b}}$

23. Diffusion

- Fick's law: flux of partiles is $\mathbf{\Phi} = -D\boldsymbol{\nabla} n^*$, $\boxed{D = \frac{1}{3}\lambda\langle v\rangle} = \frac{2}{3n^*\sigma}\sqrt{\frac{kT}{\pi m}}$ (n^* is particle of interest, $n^* \ll n$)
- $\eta = Dnm = D\rho$
- $D \propto 1/p$, $D \propto T^{3/2}$, $D \propto 1/(\sigma\sqrt{m})$

24.

Viscosity	$\Pi_z = -\eta\frac{\partial\langle v_x\rangle}{\partial z}$	$\frac{D\mathbf{v}}{Dt} = \frac{\eta}{\rho}\nabla^2\mathbf{v}$	$\eta = \frac{1}{3}nm\lambda\langle v\rangle$
Thermal conductivity	$J_z = -\kappa\frac{\partial T}{\partial z}$	$\frac{\partial T}{\partial t} = D\nabla^2 T$	$\kappa = \frac{1}{3}C_V\lambda\langle v\rangle$
Diffusivity	$\Phi_z = -D\frac{\partial n^*}{\partial z}$	$\frac{\mathrm{d}n^*}{\mathrm{d}t} = D\nabla^2 n^*$	$D = \frac{1}{3}\lambda\langle v\rangle$

25.

$\propto$	η	κ	D
$p^{(\cdot)}$	0	0	-1
$T^{(\cdot)}$	1/2	1/2	3/2
$m^{(\cdot)}$	1/2	1/2	-1/2
$d^{(\cdot)}$	-2	-2	-2

Proofs

1. ★ Reciprocity relation
   - $x = x(y,z)$, $\mathrm{d}x = \left(\frac{\partial x}{\partial y}\right)_z \mathrm{d}y + \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z$
   - $z = z(y,z)$, $\mathrm{d}x = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y$
   - $\mathrm{d}x = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left[\left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x\right] \mathrm{d}y$
   - $\left(\frac{\partial x}{\partial z}\right)_y = 1/\left(\frac{\partial z}{\partial x}\right)_y$
   - $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$
2. ★ Surface tension

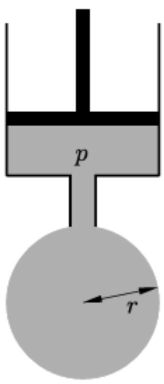
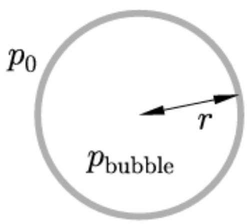


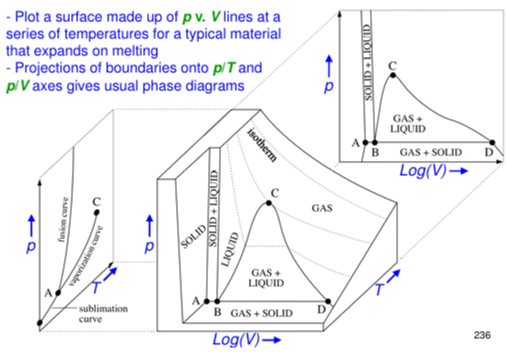
Fig. 17.3 A spherical droplet of liquid of radius r is suspended from a thin pipe connected to a piston, which maintains the pressure p of the liquid.



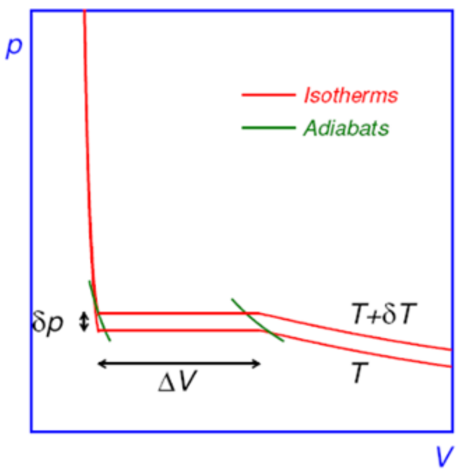
   - $\mathrm{d}W = \gamma\mathrm{d}A = p\mathrm{d}V$
   - $\mathrm{d}A = \frac{\mathrm{d}A}{\mathrm{d}r}\mathrm{d}r = 8\pi r\mathrm{d}r$
   - $\gamma(8\pi r)\mathrm{d}r = p(4\pi r^2)\mathrm{d}r$
   - $p = 2\gamma/r$
   - Pressure inside bubble is $p_0 + \frac{4\gamma}{r}$ (2 surfaces, assuming thin bubble, both walls have radius r)
3. ★
   - U, V, N, S are extensive
   - $\lambda U(S,V,N) = U(\lambda S, \lambda V, \lambda N)$ (Euler's homogeneous...)

- $\left.\frac{\partial}{\partial \lambda}\right|_{\lambda=1}$ on both sides, $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$
- $U = \left(\frac{\partial U}{\partial \lambda S}\right)_{V,N} \left(\frac{\partial \lambda S}{\partial \lambda}\right)_{+} \cdots = TS - pV + \mu N$
- $U - TS + pV = G = \mu N$
- $U - TS - \mu N = -pV = \Phi_G$
- $\boxed{\mu = G/N}$
- $\boxed{\Phi_G = -pV}$
- U, H, F, G are extensive, S, V, N are extensive, T, p, μ are intensive
- $\lambda H(T, p, N) \neq H(\lambda T, \lambda V, \lambda N)$
- $\lambda F(T, V, N) \neq F(\lambda T, \lambda p, \lambda N)$
- $\lambda G(T, p, N) \neq G(\lambda T, \lambda p, \lambda N)$
- $\lambda \Phi_G(T, V, \mu) \neq \Phi_G(\lambda T, \lambda V, \lambda \mu)$
- (The conjugate variable of a extensive variable is an intensive variable ($S - T$, $V - p$, $x - f$, $N - \mu$), natural variables of U are extensive)

4. ★ Gibbs-Duhem
   - $G = \mu N$, $\mathrm{d}G = \mu\mathrm{d}N + N\mathrm{d}\mu$
   - $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}N$
   - $N\mathrm{d}\mu = -S\mathrm{d}T + V\mathrm{d}p$

5. ★ Clausius-Clapeyron equation
   - 

     Phase boundary in p, V, T
   - Proof 1: carnot engine working between 2 phases

     –
     – $\eta = \frac{W}{L} = \frac{\delta T}{T}$
     – Maxwell's construction: isobaric during phase change, $W = p_1 \Delta V - p_2 \Delta V = \delta p \Delta V$

- $L = T\Delta S$
- $\eta = \dfrac{\delta T}{T} = \dfrac{\delta p}{T}\dfrac{\Delta V}{\Delta S}$
- $\dfrac{\mathrm{d}p}{\mathrm{d}T} = \dfrac{\Delta S}{\Delta V} = \dfrac{L}{T\Delta V}$

- Proof 2: Maxwell's relation for F
  - $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$
  - $\dfrac{\mathrm{d}p}{\mathrm{d}T} = \dfrac{\Delta S}{\Delta V} = \dfrac{L}{T\Delta V}$
- Proof 3: Gibbs-Duhem
  - In equilibrium, $\mathrm{d}G = \mu_1\mathrm{d}N_1 + \mu_2\mathrm{d}N_2 = (\mu_1 - \mu_2)\mathrm{d}N_1 = 0$, $\mu_1 = \mu_2$
  - $\mathrm{d}\mu_1 = \mathrm{d}\mu_2$
  - Gibbs-Duhem $\dfrac{-S_1\mathrm{d}T + V_1\mathrm{d}p}{N_1} = \dfrac{-S_2\mathrm{d}T + V_2\mathrm{d}p}{N_2}$
  - $-s_1\mathrm{d}T + v_1\mathrm{d}p = -s_2\mathrm{d}T + v_2\mathrm{d}p$
  - $\dfrac{\mathrm{d}p}{\mathrm{d}T} = \dfrac{s_1 - s_2}{v_1 - v_2} = \dfrac{\Delta S}{\Delta V}$

6. ★ Temperature dependence of latent heat L, assuming ideal gas

- $\Delta S = L/T$
- $\dfrac{\mathrm{d}\Delta S}{\mathrm{d}T} = \left(\dfrac{\partial \Delta S}{\partial T}\right)_p + \left(\dfrac{\partial \Delta S}{\partial p}\right)_T \dfrac{\mathrm{d}p}{\mathrm{d}T}$
- $\left(\dfrac{\partial \Delta S}{\partial T}\right)_p = \Delta\left(\dfrac{\partial S}{\partial T}\right)_p = \dfrac{C_{p,vap} - C_{p,liq}}{T}$
- $\left(\dfrac{\partial \Delta S}{\partial p}\right)_T \dfrac{\mathrm{d}p}{\mathrm{d}T} = \Delta\left[\left(\dfrac{\partial S}{\partial p}\right)_T\right]\dfrac{\mathrm{d}p}{\mathrm{d}T} = \Delta\left[\left(\dfrac{\partial V}{\partial T}\right)_p\right]\dfrac{\mathrm{d}p}{\mathrm{d}T} = \dfrac{nR}{p} \times \dfrac{L}{T\Delta V} \approx \dfrac{nRL}{pTV_{\text{gas}}} = \dfrac{L}{T^2}$
- $\dfrac{\mathrm{d}\Delta S}{\mathrm{d}T} = \dfrac{\mathrm{d}L/T}{\mathrm{d}T} = \dfrac{1}{T}\dfrac{\mathrm{d}L}{\mathrm{d}T} - \dfrac{L}{T^2}$
- $\dfrac{\mathrm{d}L}{\mathrm{d}T} = C_{p,vap} - C_{p,liq}$
- $L = L_0 + (C_{p,vap} - C_{p,liq})T$

7. ★ Bose integral

- Riemann zeta function $\zeta(s) = \displaystyle\sum_{n=1}^{\infty}\frac{1}{n^s}$
- Gamma function $\Gamma(n) = \displaystyle\int_0^{\infty} x^{n-1}e^{-}y\mathrm{d}y$
-

s	$\zeta(s)$
1	∞
2	$\pi^2/6$
4	$\pi^4/90$
6	$\pi^6/945$

- $\displaystyle\int_0^{\infty}\frac{x^n}{e^x - 1}\mathrm{d}x$
- $\displaystyle\int_0^{\infty}\frac{x^n e^{-x}}{1 - e^{-x}}\mathrm{d}x$
- $\displaystyle\int_0^{\infty} x^n e^{-x}\sum_{k=0}^{\infty} e^{-kx}\mathrm{d}x$
- $\displaystyle\left(\sum_{k=0}^{\infty}\frac{1}{(k+1)^{n+1}}\right)\left(\int_0^{\infty} y^n e^{-y}\mathrm{d}y\right)$
- $\zeta(n+1)\Gamma(n+1)$