

Statistical Physics

Objective is to understand macroscopic behaviour of a system with many particles ($\sim 10^{23}$) e.g. P, T, V, S

Microcanonical ensemble

- Consider an isolated N -particle system (N large) with fixed energy E .
 - ↳ instantaneously obeys $H|\psi\rangle = E|\psi\rangle$, where $|\psi\rangle$ is the **microstate**, describing every particle's behaviour.
 - ↳ a macro system can be made of many microstates with the same energy.
- Fundamental assumption: in equilibrium, all accessible microstates are equally likely
 - ↳ equilibrium \rightarrow steady state with constant macro quantities
 - ↳ accessible \rightarrow can be reached by small perturbs. (at fixed E)
- $\Omega(E)$ counts the number of states with energy E
- Entropy: $S(E) = k_B \ln \Omega(E)$
 - ↳ if we combine systems with E_1, E_2 , $\Omega(E_1, E_2) = \Omega(E_1)\Omega(E_2)$
 - ⇒ entropy is additive: $S(E_1, E_2) = S(E_1) + S(E_2)$
 - ↳ $S \propto N$ so it is an **extensive quantity** rule of thumb: imagine combining 2 identical systems

2nd law of thermodynamics

- Consider two isolated systems with $E_1, E_2 \rightarrow$ bring together and allow them to exchange energy. $E_{\text{tot}} = E_1 + E_2$ is fixed.
- Total num states is $\Omega_1(E_1)\Omega_2(E_2)$ summed across every possible value of $E_i \in \{E_i\}$

$$\begin{aligned} \hookrightarrow \Omega(E_{\text{tot}}) &= \sum_{\{E_i\}} \Omega_1(E_i) \Omega_2(E_{\text{tot}} - E_i) \\ &= \sum_{\{E_i\}} \exp\left(\frac{S_1(E_i)}{k_B} + \frac{S_2(E_{\text{tot}} - E_i)}{k_B}\right) \end{aligned}$$

- ↳ the sum will be dominated by the $E_i = E^*$ that maximizes the exponent. $\frac{\partial S_1}{\partial E}|_{E=E^*} - \frac{\partial S_2}{\partial E}|_{E=E_{\text{tot}}-E^*} = 0$
- ↳ $S(E_{\text{tot}}) = k_B \ln \Omega(E_{\text{tot}}) \approx S_1(E^*) + S_2(E_{\text{tot}} - E^*)$, but $S_1(E^*) + S_2(E_{\text{tot}} - E^*) \geq S_1(E_1) + S_2(E_2)$ by def. of E^*
- $\Rightarrow S(E_{\text{tot}}) \geq S_1(E_1) + S_2(E_2)$ \leftarrow 2nd law

Temperature

- Define as $\frac{1}{T} \equiv \frac{\partial S}{\partial E}$. This satisfies 0th law (no energy transfer between equal temps):
 - ↳ $T_1 = T_2 \Rightarrow \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \rightarrow$ this is the condition for max entropy
 - ↳ entropy already maximized \Rightarrow no energy transfer.
- If $T_1 \neq T_2$, there will be an energy transfer
 - ↳ $\delta S = \frac{\partial S_1}{\partial E}|_{E=E_1} \delta E_1 + \frac{\partial S_2}{\partial E}|_{E=E_2} \delta E_2$
 $= \delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) > 0$
 - ↳ so if $T_1 > T_2$, $\delta E_1 < 0$ (hot \rightarrow cold)

- T can be negative if $S \downarrow$ as $E \uparrow$, e.g. spin systems

↳ in practice, these systems are coupled with surroundings with $T > 0$

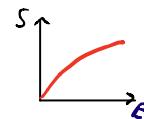
↳ negative T 'hotter' than infinite T

- The heat capacity (at constant volume) is $C_v = \frac{\partial E}{\partial T}$

↳ allows us to relate S to measurable quantities

$$\frac{\partial S}{\partial T} = \frac{\partial S}{\partial E} \frac{\partial E}{\partial T} = \frac{C_v}{T} \Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_v(T)}{T} dT$$

↳ $\frac{\partial^2 S}{\partial E^2} = -\frac{1}{T^2 C_v}$, so if $(v > 0, S(E))$ is concave-down



- General procedure for analysing a system:

1. Count $\Omega(E)$ using combinatorics (which combinations of N_1, N_2, \dots have energy E)
2. Find $S(E)$ using the Boltzmann entropy
3. Approximate factorials with Stirling's formula: $\ln N! \approx N \ln N - N$
4. Replace N_1, N_2, \dots with N_{total} and E
5. Find temp. with $\frac{1}{T} = \frac{\partial S}{\partial E}$, and invert to get $E(T)$.

1st Law of Thermodynamics

- Num. states depends on the volume V .

↳ $S(E, V) = k_B \ln \Omega(E, V)$

↳ as before $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$

↳ we define pressure to be $T \left(\frac{\partial S}{\partial V}\right)_E$

- Consider bringing together systems with p_1, p_2 (same T) with a movable partition (but $V_{\text{tot}} = \text{const}$)



↳ maximizing entropy: $\frac{\partial S_1}{\partial V} \Big|_{V=V_1} = \frac{\partial S_2}{\partial V} \Big|_{V=V_2} \Rightarrow p_1 = p_2$

↳ agrees with physical intuition.

- Use definitions of T, P to derive the 1st law:

$$S = S(E, V) \Rightarrow dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV$$

$$\Rightarrow dE = T dS - P dV$$

heat transferred to system

at fixed temperature

microcanonical had fixed energy

Canonical Ensemble

- Consider an ensemble in thermal eq. with large reservoir R with temp. T

↳ sys has negligible energy compared to R

↳ energy of system is no longer fixed



- Let $|n\rangle$ be a state of sys with energy E_n . The num. of microstates

in $\text{sys}+R$ can be found by summing over states (not energies like before)

$$\begin{aligned} \Omega(E_{\text{tot}}) &= \sum_n \Omega_R(E_{\text{tot}} - E_n) \\ &= \sum_n \exp\left[\frac{1}{k_B} S_R(E_{\text{tot}} - E_n)\right] \end{aligned}$$

↳ but $E_{\text{tot}} \gg E_n$ so we can Taylor expand $S_R(E_{\text{tot}} - E_n)$

$$\begin{aligned} \Rightarrow \Omega(E_{\text{tot}}) &= \sum_n \exp\left[\frac{1}{k_B} (S_R(E_{\text{tot}}) - \frac{\partial S}{\partial E}|_{E=E_{\text{tot}}} E_n)\right] \\ &= \exp\left[\frac{S_R(E_{\text{tot}})}{k_B}\right] \sum_n \exp(-\frac{E_n}{k_B T}) \end{aligned}$$

- The probability that sys is in state $|n\rangle$ is:

$$P(n) = \frac{\text{num states with } E_n}{\text{total num states}} \Rightarrow P(n) = \frac{e^{-E_n/k_B T}}{\sum_m e^{-E_m/k_B T}} = \frac{1}{Z(\beta)} e^{-\beta E_n}$$

- ↳ this is the Boltzmann distribution.
- ↳ $\beta = \frac{1}{k_B T}$ and $Z(\beta) = \sum_m e^{-\beta E_m}$ is the partition function
- ↳ if $\beta E_n \gg 1$, $p(n)$ is small. VERY USEFUL.
- ↳ if $\beta E_n \ll 1$, $p(n)$ is closer to 1.
- The partition function of a combined system is the product of the subsystem's: $Z = \sum_{n,m} \exp(-\beta E_n^{(1)} - \beta E_m^{(2)}) = \sum_n e^{-\beta E_n^{(1)}} \sum_m e^{-\beta E_m^{(2)}} = Z_1 Z_2$
- Energy in the canonical ensemble:
 - ↳ $\langle E \rangle = \sum_n p(n) E_n = \frac{1}{Z} \sum_n E_n e^{-\beta E_n} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \Rightarrow \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$
 - ↳ similarly, $(\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}$
 - ↳ the heat capacity is $C_V = \frac{\partial \langle E \rangle}{\partial T} = (\Delta E)^2 / k_B T^2$
- $C_V \propto (\Delta E)^2$ is extensive $\Rightarrow \Delta E \propto \sqrt{N}$.
- ↳ energy is extensive: $\Rightarrow \frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}}$
- ↳ in the thermodynamic limit ($N \rightarrow \infty$), $\frac{\Delta E}{E} \rightarrow 0$, i.e. the fluctuations around the avg are small
- ↳ we thus write $\langle E \rangle = E$
- ↳ in this limit, canonical \leftrightarrow microcanonical ensembles are equivalent.

Gibbs Entropy

- $S = k_B \ln \Omega$ is only true in the microcanonical ensemble.
- Trick to derive S for a general system: consider a micro ensemble consisting of W copies of the system ($W \gg 1$)
 - ↳ $p(n)W$ systems have state $|n\rangle$
 - ↳ no. of arrangements of states among copies: $\Omega = \frac{W!}{\prod(p(n)W)!}$

- ↳ $S_W = k_B \ln \Omega = -k_B W \sum_n p(n) \ln p(n)$ (Stirling)
- ↳ entropy is additive \therefore for one system, $S = \frac{S_W}{W}$
- ↳ gives $S = -k_B \sum_n p(n) \ln p(n)$ ← Gibbs entropy (aka. Shannon, von Neumann)

Free energy

- When $T=0$, the ground state minimises energy.
- Generally, the most likely state minimises the Helmholtz free energy
 - ↳ $F = E - TS$
 - ↳ F is the capacity to do work (at fixed temperature).
- Proof:
 - ↳ prob. that system has energy E is $P(E) = \underbrace{\Omega_s(E)}_{\text{num. of states with energy } E} \underbrace{e^{-E/k_B T}}_{\text{prob. of being in state}}$
 - ↳ $P(E) = \frac{1}{Z} e^{S(k_B)} e^{-E/k_B T} = \frac{1}{Z} e^{-\beta E}$
 - ↳ so to maximise $P(E)$, minimise F .
 - F is a Legendre transformation of $S(E, V)$:
 - ↳ $F = E - TS \Rightarrow dF = dE - TdS = -SdT - pdV$
 - ↳ most natural to consider $F = F(T, V) \Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V, P = -\left(\frac{\partial F}{\partial V}\right)_T$
 - Can show that $F = -k_B T \ln Z \Rightarrow Z = e^{-\beta F}$

Chemical Potential

- In some systems, num particles N may change (e.g. permeable membrane)
 - $\hookrightarrow S(E, V, N) = k_B \ln \Omega(E, V, N)$
 - define the chemical potential to be $\mu = -T \frac{\partial S}{\partial N}$
 - $\mu_1 = \mu_2$ in equilibrium
- The 1st law becomes $dE = TdS - pdV + \mu dN$
 - i.e. μ is the energy cost of adding a particle at fixed S, V
 - $\Rightarrow \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$
 - Helmholtz free energy: $dF = -SdT - pdV + \mu dN$

Extensive vs Intensive quantities

- Extensive quantities scale with the size of the system
 - e.g. N, V, E, S
 - for each of these, can write $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$, $\lambda \in \mathbb{R}$
- Intensive quantities are independent of size, e.g. $\frac{1}{V} = \frac{\partial S}{\partial E}$, $P = T \frac{\partial V}{\partial N}$, $\mu = -T \frac{\partial S}{\partial N}$
- Extensive \times intensive = extensive
 - e.g. $F = E - TS$ is extensive $\Rightarrow F(T, \lambda V, \lambda N) = \lambda F(T, V, N)$
 - many functional forms satisfy this, e.g. $F \sim V^{n+1}/N^n$
- $\Phi = F - \mu N$ is extensive $\Rightarrow \Phi(T, \lambda V, \lambda N) = \lambda \Phi(T, V, N)$
 - unlike for F , this is only true if $\Phi \propto V$
 - but $\left(\frac{\partial \Phi}{\partial V}\right)_{T, \mu} = -P \Rightarrow \boxed{\Phi = -P(T, \mu) V}$

Grand Canonical Ensemble

- The Grand Canonical Ensemble is in thermodynamic eq with a large reservoir of fixed μ and T
 - particle num. can now fluctuate in addition to energy.
 - reservoir much larger than system
- Prob. that system is in microstate $|n\rangle$ with E_n, N_n is:

$$\rho(n) = \frac{1}{Z(T, \mu, V)} e^{-\beta(E_n - \mu N_n)}, \quad Z = \sum_n e^{-\beta(E_n - \mu N_n)}$$

- Z is the grand partition function, from which other quantities can be derived
 - $\langle E \rangle - \mu \langle N \rangle = -\frac{\partial}{\partial \mu} \ln Z, \quad \langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z$
- All three canonical ensembles coincide in the thermodynamic limit.
- The grand canonical potential is $\Phi = F - \mu N \Rightarrow d\Phi = -SdT - pdV - N\omega\mu$
 - $\hookrightarrow \Phi = -k_B T \ln Z \Rightarrow Z = e^{-\beta \Phi}$ ← same form as canonical with F .

Classical Gases

- The quantum partition func is $Z = \sum_{\text{states}} e^{-\beta E_n}$
- Classically, specify state with phase space coordinates of every particle
 - for a single particle $H = \frac{1}{2m} |\mathbf{p}|^2 + V(\mathbf{q})$
 - this gives $Z_1 = \frac{1}{(2\pi\hbar)^3} \int d^3q d^3p e^{-\beta H}$ ← derive from QM
- An ideal gas is N non-interacting particles in a box
 - $H = |\mathbf{p}|^2/2m \Rightarrow Z_1(V, T) = \frac{1}{(2\pi\hbar)^3} \int d^3q d^3p \exp\left[-\frac{\beta H p^2}{2m}\right]$
 - $= V \left(\frac{\kappa_B T m}{2\pi k_B^2}\right)^{3/2} \equiv \frac{V}{\lambda^3}$
 - λ is the thermal de Broglie wavelength.
 - the partition function is then $Z(N, V, T) = V^N / \lambda^{3N}$
- Pressure: $p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{2}{3} k_B T \ln Z = \frac{N k_B T}{V}$ ← ideal gas law
- Energy: $\langle E \rangle = -\frac{\partial F}{\partial \mu} \ln Z = \frac{3}{2} N k_B T$
- equipartition theorem: classical systems have $\frac{1}{2} k_B T$ avg energy per degree of freedom.
- Heat capacity: $C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2} N k_B$
- We assumed $Z = Z_1^N$. This overcounts, because quantum particles are indistinguishable.

$$Z_{\text{ideal}}(N, V, T) = \frac{Z_1^N}{N!} = \frac{V^N}{N \lambda^{3N}}$$
- doesn't change P or E , but affects entropy:

$$S = \frac{\partial}{\partial T} (k_B T \ln Z) = N k_B \left[\frac{5}{2} + \ln \left(\frac{V}{N \lambda^3} \right) \right]$$
 ← Sackur-Tetrode equation
- without the $N!$, entropy is not extensive → the Gibbs paradox

The partition function can be thought of as $\sum_{\text{speeds}} \text{prob(speed)}$

For a single particle: $Z_1 = \frac{1}{(2\pi\hbar)^3} \int d^3q d^3p e^{-\beta p^2/2m}$
 $= \frac{m^3 V}{(2\pi\hbar)^3} \int dv \underbrace{v^2 e^{-\beta m v^2/2}}_{\text{prob. dist}}$

Maxwell distr.: $f(v)dv \propto v^2 e^{-mv^2/2k_B T}$

Ideal gas in the Grand canonical ensemble

$Z_{\text{ideal}}(M, V, T) = \sum_{N=0}^{\infty} e^{\mu M N} Z_{\text{ideal}}(N, V, T) = \exp\left(\frac{e^{\mu M} V}{\lambda^3}\right)$

Avg num particles: $N = \frac{1}{\mu} \frac{\partial}{\partial \mu} \ln Z = e^{\mu M} V / \lambda^3$
 $\lambda = k_B T \ln \left(\frac{N}{V}\right)$ ← not too close

for the gas to be classical, need $\lambda \ll (\frac{V}{N})^{1/3} \Rightarrow \mu < 0$
 to keep S fixed when we add a particle, E must decrease
 $\therefore \mu = \left(\frac{\partial F}{\partial N}\right)_{S, V} < 0$

Equation of state:

grand potential $\Phi = -k_B T \ln Z = -PV$

$PV = k_B T \frac{e^{\mu M V}}{\lambda^3} = N k_B T \rightarrow$ recovers ideal gas law

Diatomic gas

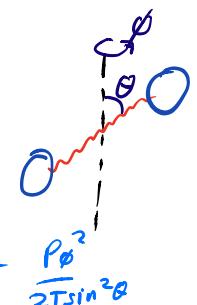
Diatomic molecules have additional degrees of freedom

Rotations: $I_{\text{rot}} = \frac{1}{2} I(\dot{\theta}^2 + \sin^2 \dot{\theta} \dot{\phi}^2)$

canonical momenta: $p_\theta = \frac{\partial I_{\text{rot}}}{\partial \dot{\theta}} = I \dot{\theta}$

$p_\phi = \frac{\partial I_{\text{rot}}}{\partial \dot{\phi}} = I \sin^2 \dot{\theta} \dot{\phi}$

Hamiltonian: $H_{\text{rot}} = \dot{\theta} p_\theta + \dot{\phi} p_\phi - L = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \dot{\theta}}$



$$\hookrightarrow Z_{\text{rot}} = \left(\frac{1}{2\pi\hbar}\right)^2 \int d\theta d\phi d\rho d\rho e^{-\beta H_{\text{rot}}} = 2I k_B T / \hbar^2$$

$\hookrightarrow \langle E_{\text{rot}} \rangle = -\frac{\partial}{\partial \beta} \ln Z_{\text{rot}} = K_B T$, i.e. rotation provides an additional 2 d.o.f \leftarrow assume $I_z=0$ along symmetry axis,

- Vibrations: model as harmonic oscillator

$$\hookrightarrow H_{\text{vib}} = \frac{p_x^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

$$\hookrightarrow Z_{\text{vib}} = \frac{1}{2\pi\hbar} \int dx dp_x e^{-\beta H_{\text{vib}}} = \frac{k_B T}{\pi\omega}$$

$\hookrightarrow \langle E_{\text{vib}} \rangle = K_B T \Rightarrow$ vibration provides 2 d.o.f

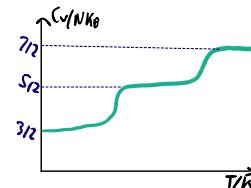
- The overall partition function is $Z_1 = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}}$

\hookrightarrow expect the heat capacity to be $C_V = \frac{3}{2} N k_B$

\hookrightarrow but experimentally we observe a changing value

\hookrightarrow at lower temps, some modes 'freeze'

\hookrightarrow this is a QM effect.



Interacting gas

- Ideal gas law is appropriate for small number densities.

- General eq. of state from the virial expansion:

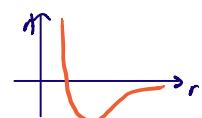
$$\frac{P}{k_B T} = \frac{N}{V} + B_2(T) \left(\frac{N}{V}\right)^2 + B_3(T) \left(\frac{N}{V}\right)^3 + \dots$$

- Objective is to compute the virial coefficients $B_i(T)$

- Model the interaction between neutral atoms with the Lennard-Jones potential

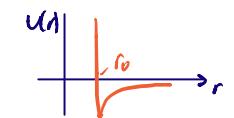
$$U(r) = \left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6$$

Pauli repulsion Van der Waals



\hookrightarrow alternatively, can we hard core repulsion

$$U(r) = \begin{cases} \infty & r < r_0 \\ -U_0 \left(\frac{r}{r_0}\right)^6 & r > r_0 \end{cases}$$



- The Hamiltonian is $H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i>j} V_{ij} \leftarrow V_{ij} \equiv U(|r_i - r_j|)$

\hookrightarrow because of the interactions, Z can't be factorised into individual particle partition funcns

$$Z(N, V, T) = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int \prod_{i=1}^N d^3 p_i d^3 r_i e^{-\beta H} = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \left[\int \prod_i d^3 r_i e^{-\beta p_i^2/2m} \right] \left[\int \prod_i d^3 r_i \exp(-\beta \sum_{j>k} U_{jk}) \right]$$

$$Z(N, V, T) = \frac{1}{N!} \frac{1}{\lambda^{3N}} \int \prod_i d^3 r_i \exp(-\beta \sum_{j>k} U_{jk})$$

- To proceed, define the Mayer F function: $f(r) = e^{-\beta U(r)} - 1$

$\hookrightarrow f(r) \rightarrow 0$ as $r \rightarrow \infty$

$\hookrightarrow f(r) \rightarrow -1$ as $r \rightarrow 0$ (avoids singularity)

$$\Rightarrow Z(N, V, T) = \frac{1}{N!} \frac{1}{\lambda^{3N}} \int \prod_i d^3 r_i \underbrace{\prod_{j>k} (1 + f_{jk})}_{1 + \sum_{j>k} f_{jk} + \sum_{l>m} f_{jkl} f_{lm} + \dots}$$

$$\hookrightarrow \int \prod_i d^3 r_i 1 = V^N$$

$\hookrightarrow \int \prod_i d^3 r_i f_{jk} = V^{N-1} \int d^3 r f(r)$, after changing to relative coordinates with $r = r_j - r_k$

\hookrightarrow independent of j, k and there are $\sim \frac{1}{2} N^2$ pairs

$$\Rightarrow Z(N, V, T) = \frac{V^N}{N! \lambda^{3N}} \left(1 + \frac{1}{2} \frac{N^2}{V^2} \int d^3 r f(r) + \dots \right)$$

- Can thus write the 2nd order partition func as:

$$Z(N, V, T) = Z_{\text{ideal}} \left(1 + \frac{N}{2V} \int d^3r f(r) \right)^N$$

↳ free energy $\rightarrow F = -k_B T \ln Z = F_{\text{ideal}} - N k_B T \ln \left(1 + \frac{N}{2V} \int d^3r f(r) \right)$

↳ can find other quantities using $\ln(1+x) \approx x$

↳ $p = -\frac{\partial F}{\partial V} \Rightarrow \frac{pV}{Nk_B T} = 1 - \frac{N}{2V} \int d^3r f(r) + \dots$
 $\Downarrow \times$ virial coefficient $B_2(T)$

for a repulsive force, $V(r) > 0 \Rightarrow f(r) < 0$, so pressure increases.

- Using the hard-core repulsion model at high temperatures, we get

the van der Waals equation of state $k_B T = (p + \frac{N^2}{V^2} a)(\frac{V}{N} - b)$

↳ can rewrite as $p = \frac{Nk_B T}{V-6N} - a \frac{N^2}{V^2}$
↳ reduced vol. due to repulsion ↳ reduced p due to attraction

↳ $b = 2\pi r_0^3/3 \approx$ excluded volume. The extra factor
 $\propto 1/2$ comes from considering config space

↳ add atoms one at a time: $\frac{1}{N!} V(V-V_{\text{exc}})(V-2V_{\text{exc}})\dots(V-NV_{\text{exc}})$.



Quantum Gases

- Consider gas in a cubic box ($V=L^3$) with periodic B.Cs

For non-interacting particles, $\Psi = \frac{1}{\sqrt{V}} e^{i \frac{k_i}{L} \cdot \vec{x}}$ with $k_i = \frac{2\pi}{L} n_i$, $n_i \in \mathbb{Z}$

↳ non-relativistic particles: $E_n = \frac{\hbar^2 k^2}{2m} = \frac{4\pi^2 \hbar^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2)$

↳ $\beta E_n = \frac{n^2 \lambda^2 \hbar^2}{L^2} \rightarrow L \gg \lambda$ so energy levels are finely spaced.

↳ approximate sums as integrals: $\sum n \approx \int d^3n = \frac{V}{(2\pi)^3} \int d^3k$

↳ in spherical coordinates in k -space, $\int d^3k = 4\pi \int_0^\infty dk k^2$

↳ the state density $g(E)$ is such that $g(E)dE$ is the num. of states with energy $E \rightarrow E+dE$.

↳ $\int d^3n = \int_0^\infty g(E)dE \Rightarrow g(E) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$

For relativistic systems, $E = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4} \Rightarrow g(E) = \frac{V E}{2\pi^2 \hbar^3 c^3} \sqrt{E^2 - m^2 c^4}$

↳ for massless particles, $g(E) = \frac{V}{2\pi^2 \hbar^3 c^3} E^2$

Photon gas

- A gas of photons at fixed T is called **black-body radiation**

$E = \hbar\omega$, with $\lambda = \frac{2\pi c}{\omega} \Rightarrow g(E)dE = 2 \cdot \frac{VE^2}{2\pi^2 \hbar^3 c^3}$ polarisations

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

↳ photons are not conserved \Rightarrow photon num not fixed. must sum over N in partition func.

For fixed ω , $Z_\omega = \sum_{N=0}^{\infty} e^{-N\beta \hbar\omega} = (1 - e^{-\beta \hbar\omega})^{-1}$

↳ overall partition func: $Z = Z_1 Z_2 \dots Z_N \Rightarrow \ln Z = \sum \ln Z_i = \int \ln z_i$

$\ln Z = \int_0^\infty d\omega g(\omega) \ln Z_\omega = \frac{-V}{\pi^2 c^3} \int_0^\infty d\omega \omega^3 \ln(1 - e^{-\beta \hbar\omega})$

↳ energy: $E = -\frac{\partial}{\partial \beta} \ln Z = \frac{V \hbar}{\pi^2 c^3} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta \hbar\omega} - 1}$

• Planck distribution: $E(\omega)d\omega = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega}-1} d\omega$

↳ max when $\frac{dE}{d\omega} = 0 \Rightarrow \omega_{\text{max}} = \frac{\hbar}{T}$ ← Wien's law

↳ total energy density: $E = \frac{E}{V} = \frac{\pi^2 k_B^4}{15 \hbar^3 c^3} T^4$

• Energy flux from a point on the surface:

↳ $\Sigma \cdot \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi/2} (\cos\theta) \sin\theta d\theta = \frac{\Sigma c}{4}$
normal component.

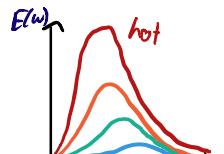
↳ gives the Stefan-Boltzmann law: Flux $= \frac{\Sigma c}{4} = \sigma T^4$

• Classically, the world is continuous $\Rightarrow \hbar\omega \ll k_B T$

↳ $\frac{1}{e^{\beta\hbar\omega}-1} \approx \frac{1}{\beta\hbar\omega} \Rightarrow E(\omega) \propto \frac{\omega^2 k_B T}{\pi^2 c^3}$

↳ this is the Rayleigh-Jeans law (classical)

↳ leads to the ultraviolet catastrophe because it diverges at small λ



Debye Model of Phonons

• Vibrations in a solid come in discrete packets of energy - phonons

↳ $E = \hbar\omega \approx \hbar|k|c_s$ ← valid for small $|k|$ linear approx to dispersion relation

↳ phonons have 3 polarisations: 2 transverse + 1 longitudinal

↳ density of states $g(\omega) = 3 \cdot \frac{\omega^2}{2\pi^2 c_s^3}$

↳ minimum wavelength is lattice spacing \rightarrow max freq ω_D Debye freq.

• The Debye model determines ω_D :

↳ equate the num. of single phonon states with the d.o.f (both count the num. of possible excitations)

↳ $3N = \int_0^{\omega_D} g(\omega) d\omega = \frac{V\omega_D^3}{2\pi^2 c_s^3} \Rightarrow \omega_D = c_s (6\pi^2)^{1/3} \left(\frac{N}{V}\right)^{1/3}$

↳ can associate a characteristic energy/temp with ω_D

• The Debye temperature is $K_B T_D = \hbar\omega_D$

↳ temp. at which the highest freq phonon becomes excited

↳ $T_D \sim$ hundreds of kelvin (higher for harder materials).

• Phonons are not conserved \Rightarrow similar partition func to photons

↳ $Z_\omega = (1 - e^{-\beta\hbar\omega})^{-1}$ (same as photon)

↳ $\ln Z_{\text{phon}} = \int_0^{\omega_D} d\omega g(\omega) \ln Z_\omega$ (integrate up to ω_D , not ∞)

↳ $\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$

$$= \frac{3V\hbar}{2\pi^2 c_s^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\beta\hbar\omega}-1} d\omega = \frac{3V}{2\pi^2 (K_B T)^3} (K_B T)^4 \int_0^{T_D/T} \frac{x^3}{e^x-1} dx$$

• For low temp ($T \ll T_D$), $C_V \propto T^3$. This explains the Dulong-petit law, which previous models failed to predict.

• For high temp $C_V \rightarrow 3Nk_B$ as required.

• In most materials the heat capacity is dominated by phonon modes.

Diatomic gas (QM correction)

• The classical $C_V = \frac{3}{2} Nk_B$ only agrees with experiment for high T because d.o.f.s 'freeze out' at lower temp.

• e.g. for rotation, $E = \frac{\hbar^2}{2I} j(j+1)$, $j = 0, 1, 2, \dots$ with degen $2j+1$

↳ $Z_{\text{rot}} = \sum_{j=0}^{\infty} (2j+1) \exp(-\beta\hbar^2 j(j+1)/2I)$

↳ when $T \gg \hbar^2/2Ik_B$, sum \rightarrow integral $\therefore Z_{\text{rot}} \approx \frac{2I}{\beta\hbar^2}$ same as classical

↳ but for $T \ll \hbar^2/2Ik_B$, $Z_{\text{rot}} \approx 1$ so rotational modes are 'frozen'.

• Similar analysis for vibrational modes with $E = \hbar\omega(n+\frac{1}{2})$.

Bose-Einstein Distribution

- Bosons have exchange-symmetric wavefunctions: $\Psi(\underline{r}_1, \underline{r}_2) = \Psi(\underline{r}_2, \underline{r}_1)$
- Label single-particle states such that $H|\underline{r}\rangle = E_r |\underline{r}\rangle$, with n_r particles in each $|\underline{r}\rangle$
- Canonical ensemble: sum over sets $\{n_r\}$ s.t. $\sum_r n_r = N$
 $Z = \sum_{\{n_r\}} e^{-\beta n_r E_r}$ ← difficult because of $\{n_r\}$
- Easier to work in grand canonical. For a given state $|\underline{r}\rangle$:
 $Z_r = \sum_{n_r} e^{-\beta n_r (E_r - \mu)} = (1 - e^{-\beta(E_r - \mu)})^{-1}$
- ↳ converges for $E_r - \mu > 0$ for all states. $E_0 = 0 \Rightarrow \mu < 0$
- ↳ state occupations are independent of each other:

$$Z_{\text{grand}} = \prod_r \frac{1}{1 - e^{-\beta(E_r - \mu)}}$$

- ↳ $\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_{\text{grand}} = \sum_r \frac{1}{e^{\beta(E_r - \mu)} - 1} = \sum_r \langle n_r \rangle$
- ↳ so the avg num of particles in $|\underline{r}\rangle$ is: $n_r = \frac{1}{e^{\beta(E_r - \mu)} - 1}$ → Bose-Einstein
Distr.
- ↳ Fugacity: $z = e^{\beta \mu}$. For boson gas, $0 < z < 1$
- Total num. of particles: $N(\mu, T, V) = \int dE n g(E) = \int dE \frac{g(E)}{z^{\beta E} - 1}$
- Pressure: $pV = \frac{1}{\beta} \ln Z_r = -\frac{1}{\beta} \int dE g(E) \ln(1 - z e^{-\beta E})$
 ↳ $g(E) \propto E^{1/2}$ so integrate by parts $pV = \frac{2}{3} \int dE \frac{E g(E)}{z^{\beta E} - 1}$
 $\Rightarrow pV = \frac{2}{3} E$

High-temperature boson gas

- Consider the $z = e^{\beta \mu} \ll 1$ limit:

$$\frac{N}{V} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty dE \frac{E^{1/2}}{z^{-1} e^{\beta E} - 1} = [\dots] \int_0^\infty dE \frac{ze^{-\beta E} E^{1/2}}{1 - ze^{-\beta E}}$$

↳ let $x = \beta E = u^2$ and expand ← Gaussian integrals

$$\Rightarrow \frac{N}{V} = \frac{3}{\pi^3} \left(1 + z \cdot \frac{1}{2\sqrt{2}} + \dots \right) (*) \quad \text{else need } z \text{ large}$$

↳ expansion only consistent if $\frac{\pi^3 N}{V} \ll 1 \Rightarrow \pi^3 \ll \frac{V}{N}$

↳ this is thus the high temp. expansion

↳ i.e. at constant N, μ must change: $\frac{N}{V} = \text{const} \Rightarrow \frac{3}{\pi^3} = \text{const}$
 $\Rightarrow Z \propto T^{-3/2}$

- To get the E & S , we need another expression for E :

$$\frac{E}{V} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty dE \frac{E^{3/2}}{z^{-1} e^{\beta E} - 1} = \dots = \frac{3z}{2\pi^3 \beta} \left(1 + \frac{3}{4\sqrt{2}} + \dots \right)$$

↳ eliminate small z using inverted (*)

$$\Rightarrow E = \frac{3}{2} \frac{N}{\beta} \left(1 - \frac{1}{2\sqrt{2}} \frac{\pi^3 N}{V} + \dots \right) \left(1 + \frac{1}{4\sqrt{2}} \frac{\pi^3 N}{V} + \dots \right)$$

$$\hookrightarrow \text{sub } pV = \frac{2}{3} E \Rightarrow pV = Nk_B T \left(1 - \frac{\pi^3 N}{4\sqrt{2} V} + \dots \right)$$

↳ at high temp, classical ideal gas is recovered

Low-temperature limit (Bose-Einstein Condensation)

- For low temp, $z \rightarrow 1$.

$$\frac{N}{V} = \frac{1}{4\pi^2} \left(\frac{2\pi k_B T}{\hbar^2} \right)^{3/2} \int_0^\infty dx \frac{x^{1/2}}{e^x - 1} \equiv \frac{1}{\lambda^3} g_{3/2}(z)$$

- $g_n(z)$ is a polylogarithm: $g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{e^x - 1}$

\hookrightarrow as $z \rightarrow 0$, $g_{3/2}(z) \rightarrow 0$

$\hookrightarrow g_n(z)$ is a monotonically increasing function of z \hookleftarrow convert integral to sum

$\hookrightarrow g_n(1) = \zeta(n)$ (Riemann zeta function)

- As $T \downarrow$ there will be some $T = T_c$ for which $z = 1$:

$$\hookrightarrow \text{sub } z=1 : \frac{N}{V} = \left(\frac{\pi k_B T_c}{2\hbar^2} \right)^{3/2} \zeta\left(\frac{3}{2}\right)$$

\hookrightarrow for $T < T_c$, it seems that $\frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(z)$ should decrease since $\Re z$, i.e. particles disappear.

- The mistake was approximating the sum over states as an integral

$\hookrightarrow \sum_n \propto \text{Sole } E^{1/2}$ gives zero weight to the ground state

\hookrightarrow as $T \downarrow$, the particles are condensing into the ground state

$\hookrightarrow f-E$ distr: $n_0 = \frac{1}{z^{-1}-1}$, so as $z \rightarrow 1$, n_0 gets large.

- Including the ground state $\frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(z) + \frac{1}{z^{-1}-1}$

$\hookrightarrow N$ is fixed as $T \rightarrow 0$

\hookrightarrow for finite N , $z \rightarrow 1 - \frac{1}{N}$ as $T \rightarrow 0$

\hookrightarrow frac. of particles in the ground state is $\frac{n_0}{N} \propto 1 - \frac{1}{N} \approx \zeta\left(\frac{3}{2}\right) = 1 - \left(\frac{T}{T_c}\right)^{3/2}$

\hookrightarrow at low T , a macroscopic num of particles may be in the ground state

\rightarrow Bose-Einstein Condensate (BEC)

$$\text{EoS: } P = \frac{2}{3} \frac{E}{V} = \frac{k_B T}{\lambda^3} g_{5/2}(z)$$

\hookrightarrow for $T < T_c$, $z \approx 1 \Rightarrow P \approx \frac{k_B T}{\lambda^3} \zeta\left(\frac{5}{2}\right) \propto T^{5/2}$ (independent of $\frac{N}{V}$)

Phase transitions

\rightarrow discontinuities in physical observables.

- BEC formation is a phase trans.

$$\text{For a boson gas, } \frac{E}{V} = \frac{3}{2} \frac{k_B T}{\lambda^3} g_{5/2}(z)$$

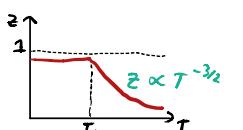
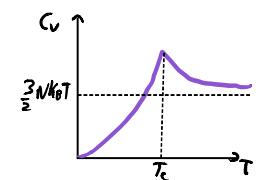
$$\Rightarrow \frac{C_V}{V} = \frac{1}{V} \frac{dE}{dT} = \frac{15k_B}{4\lambda^3} g_{5/2}(z) + \frac{3}{2} \frac{k_B T}{\lambda^3} \frac{dg_{5/2}}{dz} \frac{dz}{dT} \hookrightarrow \approx 0 \text{ for } T < T_c$$

\hookrightarrow for $T < T_c$, $\frac{C_V}{V} \sim T^{3/2}$

$\hookrightarrow C_V$ decreases for $T > T_c \Rightarrow$ max at $T = T_c$

$$\hookrightarrow C_V = \frac{15V k_B}{4\lambda^3} g_{5/2}(z) - b\left(\frac{T-T_c}{T_c}\right)$$

- This discontinuity only exists in the $N \rightarrow \infty$ limit.



Fermi-Dirac Distribution

- Wavefunction is exchange antisymmetric: $\Psi(r_1, \sigma_1) = -\Psi(r_2, \sigma_2)$
- Fermions obey Pauli exclusion \rightarrow any state occupied by 0 or 1 fermion
- A composite particle made of $2N$ fermions acts as a boson
- Work in grand canonical:
 - \hookrightarrow for a given state $Z_r = \sum_{n=0,1} e^{-\beta n(E_r - \mu)} = 1 + e^{-\beta(E_r - \mu)}$
 - $\hookrightarrow Z = \prod_r Z_r \Rightarrow \langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z = \sum_r \frac{1}{e^{\beta(E_r - \mu)} + 1} = \sum_r \langle n_r \rangle$
 - \hookrightarrow this gives the Fermi-Dirac distr.: $n_r = \frac{1}{e^{\beta(E_r - \mu)} + 1}$
 - $\hookrightarrow \mu$ can be either positive or negative.

Ideal Fermi gas

- Non-interacting, non-relativistic: $E = \frac{\hbar^2 k^2}{2m}$
- Fermions have degeneracy $g_s = 2s+1$ so the density of states is:

$$g(E) = \frac{g_s V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

- $\hookrightarrow N = \int dE \frac{g(E)}{e^{\beta(E-\mu)} + 1}, E = \int dE \frac{E g(E)}{e^{\beta(E-\mu)} + 1}$
- $\hookrightarrow pV = k_B T \ln Z \Rightarrow pV = \frac{2}{3} E$ (same as bosons)
- High-temp expansion ($z \ll 1$): $pV = Nk_B T \left(1 + \frac{2^3 N}{4\sqrt{2} g_s V} + \dots\right)$

Degenerate Fermi gas

- As $T \rightarrow 0$, $\frac{1}{e^{\beta(E-\mu)} + 1} \rightarrow \begin{cases} 1, & E < \mu \\ 0, & E > \mu \end{cases}$

\hookrightarrow each fermion goes into the lowest-energy available state until all fermions have been used up

\hookrightarrow the Fermi energy E_F is the energy of the last filled state.

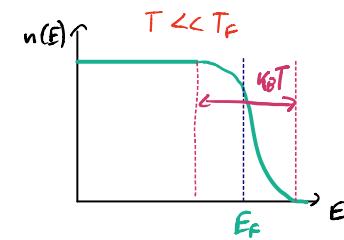
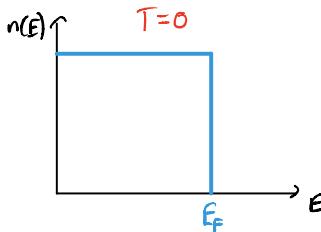
$$E_F \equiv \mu(T=0) \quad \leftarrow \text{at fixed } N$$

$$\hookrightarrow E_F \text{ in terms of } N: N = \int_0^{E_F} dE g(E) = \frac{g_s V}{6\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}$$

$$\Rightarrow E_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{g_s V}\right)^{2/3} N^{2/3}$$

- E_F is the characteristic energy scale; there is an associated characteristic Fermi temperature $T_F = \frac{E_F}{k_B}$ $\leftarrow T < T_F$ is 'low' temp
- Fermi momentum k_F : $E_F = \frac{\hbar^2 k_F^2}{2m}$
 - \hookrightarrow states with $|k| < k_F$ are filled \rightarrow Fermi sea
 - \hookrightarrow states with $|k| = k_F$ form the Fermi surface
- $T=0$ EOS: $pV = \frac{2}{3} E = \frac{2}{3} \int_0^{E_F} dE E g(E) = \frac{2}{3} N E_F$
 - \hookrightarrow pressure nonzero even at $T=0 \rightarrow$ degeneracy pressure

Low temperature Fermi gas ($T \ll T_F$)



We are interested in $E(T)$. We have $\frac{E}{V} = \frac{g_1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty dE \frac{E^{3/2}}{e^{\beta(E-\mu)} + 1}$

For N fixed, we must have $\frac{dN}{dT}|_{T=0} = 0$

$$\hookrightarrow \frac{dN}{dT} = \frac{d}{dT} \int_0^\infty dE \frac{g(E)}{e^{\beta(E-\mu)} + 1} = \int_0^\infty dE g(E) \frac{d}{dT} \left(\frac{1}{e^{\beta(E-\mu)} + 1} \right)$$

$\hookrightarrow \frac{d}{dT} [\dots]$ only nonzero (approximately) near E_F , so $g(E) \approx g(E_F)$

\hookrightarrow replace μ by E_F since T small

$$\therefore \frac{dN}{dT} \approx g(E_F) \int_0^\infty dE \left(\frac{E-E_F}{k_B T^2} \right) \frac{1}{4 \cosh^2(\beta(E-E_F)/2)} \approx 0$$

Odd about E_F Even about E_F

Heat capacity: $C_V = \frac{\partial E}{\partial T}|_{N,V} = \int_0^\infty dE E g(E) \frac{\partial}{\partial T} \frac{1}{e^{\beta(E-\mu)} + 1}$

$$\hookrightarrow \text{Taylor expand } E g(E) = E_F g(E_F) + \frac{3}{2} g'(E_F)(E-E_F)$$

$$\hookrightarrow C_V = \frac{3}{2} g(E_F) T \int_{-\infty}^\infty dx \frac{x^2}{4 \cosh^2(x/2)} \Rightarrow C_V \sim g(E_F) T \sim N k_B T / T_F$$

\hookrightarrow linear because only the fermions within $k_B T$ of E_F participate;
if each acquires energy $k_B T$, $E \sim g(E_F) k_B T \cdot k_B T \Rightarrow C_V \sim g(E_F) T$

Electrons in metals can be modelled as free Fermi gas

$$\hookrightarrow \text{heat capacity for a metal: } C_V = \underset{\text{electrons}}{\overset{T}{\propto}} + \underset{\text{phonons}}{\overset{T}{\propto}} T^3$$

\hookrightarrow phonons dominate at high T

Pauli paramagnetism

External magnetic fields cause electron spins to align:

$$E_{\text{spin}} = \mu_0 B S, \text{ where } \mu_0 = \frac{e h}{2mc} \text{ is the Bohr magneton and } S = \pm 1$$

\uparrow and \downarrow now have different occupations:

$$\frac{N}{V} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty dE \frac{1}{e^{\beta(E + \mu_0 B - \mu)} - 1}$$

Magnetisation measures how energy changes with B : $M = -\frac{\partial E}{\partial B}$

$$\hookrightarrow E = E_0 + \mu_0 B N_p - \mu_0 B N_d \Rightarrow M = -\mu_0 (N_p - N_d)$$

\hookrightarrow Magnetic susceptibility: $\chi = \frac{\partial M}{\partial B} \leftarrow$ how easy to magnetise

$$\cdot \text{At high temperatures, } z \rightarrow 0 \Rightarrow \frac{N}{V} \rightarrow \frac{2}{\pi^3} e^{-\beta \mu_0 B} \Rightarrow M \approx \frac{2\mu_0 V z}{\pi^3} \sinh(\beta \mu_0 B)$$

$$\hookrightarrow N = N_p + N_d \approx \frac{2Vz}{\pi^3} \cosh(\beta \mu_0 B) \text{ so we can eliminate } z$$

$$\Rightarrow M \approx \mu_0 N \tanh(\beta \mu_0 B) \leftarrow \text{same as classical model}$$

$$\hookrightarrow \text{susceptibility at zero field: } \chi|_{B=0} = \frac{NM^2}{k_B T} \sim \frac{1}{T} \leftarrow \text{Curie's law}$$

At low temperatures, $M \approx \mu_0^2 g(E_F) B$

$$\hookrightarrow \text{susceptibility} \rightarrow \text{constant: } \chi = \mu_0^2 g(E_F)$$

\hookrightarrow only states near the Fermi surface can flip spins

\hookrightarrow materials with $\chi > 0$ are paramagnetic

Classical Thermodynamics

The Zeroth Law

- An **insulated system** is one that is inside adiabatic walls \rightarrow isolated from external influences
- A **diathermal wall** separates systems in **thermal contact**
- Equilibrium** is a state in which macroscopic variables are constant.

• **Zeroth law:** transitivity of equilibrium

$$\begin{array}{c} A \xleftarrow{\text{eq}} C \\ B \xleftarrow{\text{eq}} C \end{array} \Rightarrow A \xleftarrow{\text{eq}} B$$

- Zeroth law defines a temperature scale:

$\hookrightarrow A, C$ in equilibrium $\Rightarrow F_{AC}(p_A, V_A; p_C, V_C) = 0 \Rightarrow V_C = f_{AC}(p_A, V_A; p_C)$

$\hookrightarrow B, C$ in equilibrium $\Rightarrow V_C = f_{BC}(p_B, V_B; p_C)$

\hookrightarrow eliminate $V_C \Rightarrow F_{AC}(p_A, V_A; p_C) = f_{BC}(p_B, V_B; p_C)$ (*)

\hookrightarrow zeroth law $\Rightarrow A, B$ in equilibrium $\Rightarrow F_{AB}(p_A, V_A; p_B, V_B)$ (†)

\hookrightarrow (†) means that we can eliminate p_C from (*). This means that $\Theta_A(p_A, V_A) = \Theta_B(p_B, V_B)$

$\hookrightarrow \Theta(p, V)$ is the **temperature**, $T = \Theta(p, V)$ is the **equation of state**.

The First Law

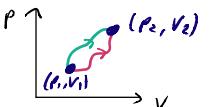
- First law:** amount of work required to change an isolated system from state 1 \rightarrow 2 is independent of how the work is performed
- There is some function of state $E(p, V) \rightarrow$ **energy**, such that $\Delta E = w$
- A non-isolated system may also gain energy via **heat transfer**

- 1st law is conservation of energy: $\Delta E = Q + W$
- A **quasi-static process** is one for which the sys. is always in equilibrium (though the 1st law can describe violent changes)
 - \hookrightarrow can write 1st law infinitesimally: $dE = dQ + dW$
 - $\hookrightarrow E$ is a func. of state so dE is a total derivative
 - \hookrightarrow however, Q, W are not functions of state, so dQ, dW only mean that the quantities are small.

- For compression, $dW = -pdV \hookrightarrow$ work done **on** system

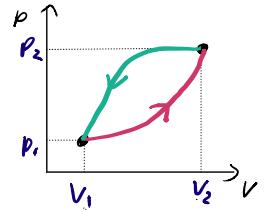
$\hookrightarrow \int dE = E(p_2, V_2) - E(p_1, V_1) \hookrightarrow$ independent of path

$\hookrightarrow \int dW = - \int_{V_1}^{V_2} pdV \hookrightarrow$ depends on path

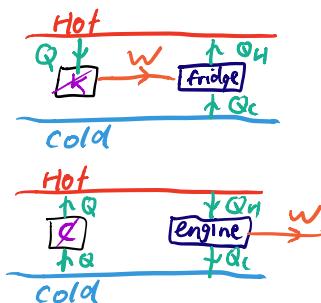


The Second Law

- reversible process** is a quasi-static process that can be run backwards
- For a closed loop on a pV diagram:
 - $\oint dE = 0$ since E is a func. of state
 - \hookrightarrow but $\oint pdV \neq 0$
 - \hookrightarrow 1st law $\Rightarrow \oint dQ = \oint pdV$
 - \hookrightarrow i.e. reversible cycles can convert heat \leftrightarrow work
- Second law (Kelvin):** no process is possible whose sole effect is to convert heat entirely into work.
- Second law (Clausius):** no process is possible whose sole effect is to transfer heat from a colder to a hotter body.
- 2nd law defines an arrow of time (e.g. Clausius \Rightarrow hot $\xrightarrow{\text{heat flow}}$ cold)



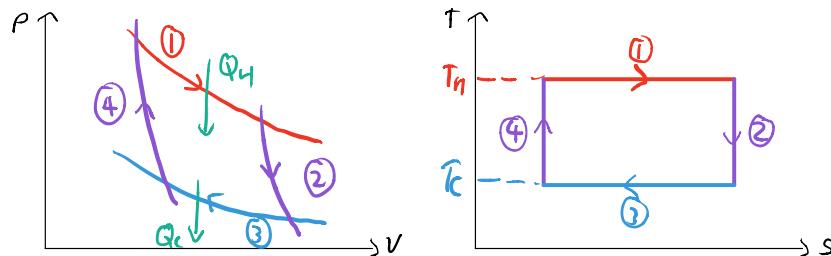
- Kelvin violator \Rightarrow Clausius violator:
net $Q_H - Q = Q_C$ transferred from cold to hot
- Clausius violator \Rightarrow Kelvin violator:



Carnot Cycle

- Reversible cycles do not violate Kelvin's 2nd law because they deposit heat.

- Carnot cycle:



- ① Isothermal expansion at T_H ; Q_H absorbed from hot res.
- ② Adiabatic expansion; $T \downarrow$
- ③ Isothermal compression at T_C ; Q_C dumped into cold res
- ④ Adiabatic compression; $T \uparrow$

- Work done is $W = Q_H - Q_C$ with efficiency

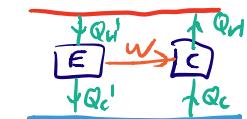
$\hookrightarrow \eta = 1$ would violate Kelvin's 2nd law

$$\eta = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

- Carnot's theorem: of all the heat engines operating between two heat reservoirs, a reversible engine has the highest efficiency

\hookrightarrow prove by coupling another engine to drive a Carnot pump

\hookrightarrow net effect is to extract $Q_H' - Q_H$ of heat. Clausius $\Rightarrow Q_H' > Q_H \Rightarrow \eta_E \leq \eta_C$



- Corollary: all reversible engines have the same efficiency $\eta(T_H, T_C)$

\hookrightarrow use a Carnot engine to drive the other engine in reverse
 $\hookrightarrow \eta_E \leq \eta_C$ and $\eta_C \leq \eta_E \Rightarrow \eta_E = \eta_C$

- The Carnot cycle defines a thermodynamic temperature scale:

\hookrightarrow let $T_1 > T_2 > T_3$ and consider 2 Carnot engines operating between T_1, T_2 and T_2, T_3 respectively

$$\hookrightarrow Q_2 = Q_1(1 - \eta(T_1, T_2)) \text{ and } Q_3 = Q_2(1 - \eta(T_2, T_3))$$

$$\Rightarrow Q_3 = Q_1(1 - \eta(T_1, T_2))(1 - \eta(T_2, T_3))$$

\hookrightarrow but can also treat as one engine between T_1, T_3

$$\therefore Q_3 = Q_1(1 - \eta(T_1, T_3))$$

$$\Rightarrow (1 - \eta(T_1, T_3)) = (1 - \eta(T_1, T_2))(1 - \eta(T_2, T_3)) \quad \begin{matrix} T_2 \text{ must} \\ \text{cancel} \end{matrix}$$

$$\Rightarrow 1 - \eta(T_1, T_3) = f(T_2)/f(T_1)$$

\hookrightarrow we can choose $f(T) = T$

- This definition of temperature coincides with the ideal gas temp:

$$\hookrightarrow \text{isotherms: } Q_H = \int_A^B p dV = \int_A^B \frac{Nk_B T}{V} dV = Nk_B T_H \ln\left(\frac{V_B}{V_A}\right)$$

$$Q_C = -Nk_B T_C \ln\left(\frac{V_0}{V_C}\right) \text{ similarly}$$

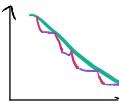
$$\hookrightarrow \text{adiabats: } dQ = 0 \Rightarrow dE = C_V dT = -pdV \Rightarrow TV^{2/3} = \text{const}$$

$$\Rightarrow V_A/V_B = V_0/V_C$$

$$\hookrightarrow \eta = 1 - \frac{Q_C}{Q_H} = 1 + \frac{T_C}{T_H} \frac{\ln(V_0/V_A)}{\ln(V_0/V_C)} = 1 - \frac{T_C}{T_H} \quad \text{agrees with Carnot.}$$

Entropy of reversible processes

- For a Carnot cycle, $Q_H/T_H = Q_C/T_C \Rightarrow \sum_i \frac{Q_i}{T_i} = 0$
- A general path can be split into infinitesimal adiabats and isotherms.
 - for a general reversible process $\oint \frac{dQ}{T} = 0$
 - this implies $\frac{dQ}{T}$ is path-independent \Rightarrow function of state
 - call this **entropy** (coincides with previous definition)
- For an irreversible engine $\frac{Q_H'}{T_H} - \frac{Q_C'}{T_C} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} + (\frac{Q_H'}{T_H} - \frac{Q_H}{T_H}) + (\frac{Q_C}{T_C} - \frac{Q_C'}{T_C}) > 0$ because of efficiency
- for a general irreversible path $\oint \frac{dQ}{T} \leq 0$ (**Clausius inequality**)
- consider paths I and II: $\oint \frac{dQ}{T} = \int_I \frac{dQ}{T} - \int_{II} \frac{dQ}{T}$
 - $\Rightarrow \int_I \frac{dQ}{T} \leq S(B) - S(A)$
 - for an isolated system $dQ=0 \Rightarrow S(B) \geq S(A)$



Thermodynamic potentials

- The state of a system can be specified using 2 of:

$p \quad V \quad E \quad T \quad S$

- each has 'natural variables', e.g. $dE = TdS - pdV \Rightarrow E = E(S, V)$
- mixed partials give Maxwell relations: $\frac{\partial^2 E}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

- Can define different potentials:

$$\begin{aligned} \hookrightarrow \text{Helmholtz: } F &= E - TS \Rightarrow dF = -SdT - pdV \\ \hookrightarrow \text{Gibbs: } G &= E + pV - TS \Rightarrow dG = -SdT + Vdp \\ \hookrightarrow \text{Enthalpy: } H &= E + pV \Rightarrow dH = TdS + Vdp \end{aligned} \quad \left. \begin{array}{l} \text{each has} \\ \text{a Maxwell} \\ \text{relation} \end{array} \right\}$$

- Mnemonic: Good Physicists Have Studied Under Very Fine Teachers

- natural variables next to potential

- differential: opposite corners for coeff, then follow diag to get differential (no sign)

- Maxwell relations: $\left[\begin{array}{c} S \\ p \end{array}\right] = \left[\begin{array}{c} V \\ T \end{array}\right]$ and rotations
e.g. $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \Rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

-S	U	V
H	F	
-p	G	T

- If particle number may vary, we must add μdN

- G is extensive $\Rightarrow G(T, p, \lambda N) = \lambda G(T, p, N)$

$$\Rightarrow G(T, p, N) = m(T, p) N \quad \left. \begin{array}{l} m \text{ is Gibbs free energy} \\ \text{per unit particle} \end{array} \right\}$$

The Third Law

- Third law: $\frac{S}{N} \rightarrow 0$ as $T \rightarrow 0$ and $N \rightarrow \infty$

- i.e. ground state entropy is not extensive

- provides an absolute reference for entropy

- Heat capacities $\rightarrow 0$ as $T \rightarrow 0$ since $S(B) - S(A) = \int_A^B dT \frac{C}{T}$

- classical ideal gases violate this

- low temperatures need QM

Phase Transitions

A phase transition is a discontinuous change in system properties

Liquid-Gas transition

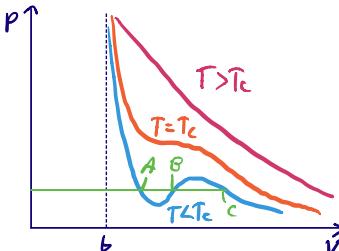
van der Waals equation: $p = \frac{k_BT}{v-b} - \frac{a}{v^2}$, using $v = \frac{N}{\rho}$

↳ shape of isotherm depends on temperature

↳ at high T , ignore $\frac{a}{v^2}$ → monotonically decreasing

↳ at $T=T_c$, there is a saddle point

$$\frac{\partial p}{\partial v} = 0, \frac{\partial^2 p}{\partial v^2} = 0 \Rightarrow k_B T_c = \frac{8a}{27b}$$



For $T < T_c$, a given pressure can correspond to several densities

↳ solution B is unstable because $(\frac{\partial p}{\partial v})_T > 0$

↳ solution A has closely-packed and is hard to compress since $|\frac{\partial p}{\partial v}|$ is large → this is a liquid

Two phases are in equilibrium when:

1. Same temp.
 2. Same pressure
 3. Same chemical potential, i.e. $\mu_{\text{liquid}} = \mu_{\text{gas}}$
- } satisfied for A, B, C since on isotherm

Equilibrium only depends on intensive quantities, so we can scale up N_{liquid} and N_{gas} .

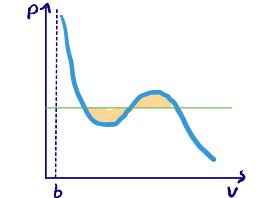
To solve $\mu_{\text{liquid}} = \mu_{\text{gas}}$, vary $\mu(p, T)$ along an isotherm

$$\begin{aligned} \text{↳ } d\mu &= \left(\frac{\partial \mu}{\partial p}\right)_T dp. \quad G(p, T, N) = \mu(p, T)N \\ dG &= -SdT + Vdp + \mu dN \Rightarrow \left(\frac{\partial \mu}{\partial p}\right)_T = \frac{1}{N} \left(\frac{\partial G}{\partial p}\right)_T \end{aligned}$$

↳ starting at μ_{liquid} and integrating, $\mu(p, T) = \mu_{\text{liquid}} + \int_{p_{\text{liquid}}}^p \frac{V(p', T)}{N} dp'$

↳ for $\mu_{\text{liquid}} = \mu_{\text{gas}}$, the integral must vanish

↳ this is the Maxwell construction → areas of shaded regions must be equal for liquid and gas to coexist

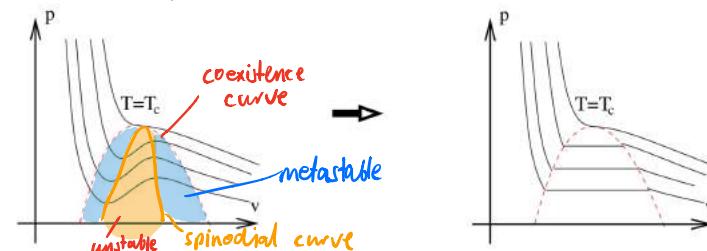


For a fixed $T < T_c$, there is a unique equilibrium pressure

↳ the set of all these pressures defines the coexistence curve

↳ inside the curve, average density may vary (between the liquid and gas densities)

↳ if we cool a particular system to a point inside the curve, it will undergo phase separation: liquid and gas coexist

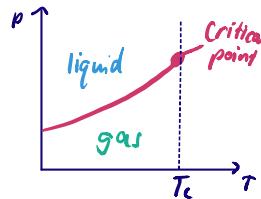


The coexistence curve encompasses the unstable regions where $(\frac{\partial p}{\partial v})_T > 0$ but also metastable regions where $(\frac{\partial p}{\partial v})_T < 0$

↳ these states (between spinodal and coexistence curves) have higher G than the liquid-gas eq, but can be reached (supercooling)

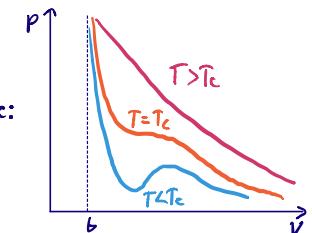
Clausius-Clapeyron equation

- On the $p-T$ plane, the co-existence curve becomes a line \rightarrow phase boundary
 - \hookrightarrow crossing the boundary involves a discontinuous change in volume.
 - \hookrightarrow for $T > T_c$ there is no distinction between liquid and gas (i.e. continuous change in volume)
- On the phase boundary, $g_L = g_g \Rightarrow \frac{G_L}{N_L} = \frac{G_g}{N_g}$
 - $\hookrightarrow dG = -SdT + Vdp \Rightarrow dg_L = -S_L dT + V_L dp$ } quantities per particle
 - $dg_g = -S_g dT + V_g dp$
 - \hookrightarrow setting $dg_L = dg_g$, we get an expression for the slope of the phase boundary: $\frac{dp}{dT} = \frac{(S_g - S_L)}{(V_g - V_L)}$
 - \hookrightarrow define the specific latent heat $L \equiv T(S_g - S_L)$
 - \hookrightarrow Clausius-Clapeyron equation:
$$\frac{dp}{dT} = \frac{L}{T(V_{\text{gas}} - V_{\text{liq}})}$$
- A phase transition is n th order if the n th derivative of a thermodynamic potential is discontinuous (Ehrenfest classification)
 - \hookrightarrow liquid-gas is 1st order: $(\frac{\partial F}{\partial T})_V, (\frac{\partial G}{\partial P})_T$ are discontinuous
 - \hookrightarrow as $T \rightarrow T_c$, $S_L \rightarrow S_g$ so the discontinuity diminishes (becomes a 2nd order transition)



The law of Corresponding States

- At the critical point, $\frac{\partial p}{\partial v} = \frac{\partial^2 p}{\partial v^2} = 0$.
- Alternate derivation \rightarrow rearrange vdW into a cubic: $pv^3 - (pb + k_BT)v^2 + av - ab = 0$
 - \hookrightarrow at $T = T_c$, the equation goes from having 3 real roots to 1, so at T_c all 3 coincide
 - $\Rightarrow p_c(v - v_c)^3 = 0$
 - $\Rightarrow k_BT_c = \frac{8a}{27b}, v_c = 3b, p_c = \frac{a}{27b^2}$
- We can rewrite the vdW equation using reduced variables $\bar{T} = T/T_c$, $\bar{v} = v/v_c$, $\bar{p} = p/p_c$ and write a, b in terms of critical quantities \rightarrow should now apply to all gases.
 - \hookrightarrow result is the Law of Corresponding States: $\bar{p} = \frac{8\bar{T}}{3\bar{v}} - \frac{3}{\bar{v}^2}$
 - \hookrightarrow universal compressibility ratio: $\frac{p_c v_c}{k_B T_c} = \frac{3}{8} = 0.375$
 - \hookrightarrow vdW overestimates compressibilities.
- Plotted in the $\bar{p}-\bar{T}$ plane, coexistence curves of many different gases coincide \rightarrow universality.



Critical exponents

- We can analyse how quantities vary near the critical point then compare with experiment.
- ① How does $v_g - v_l$ vary along the coexistence curve as $T \rightarrow T_c$?
 - \hookrightarrow Law of corresponding states gives $\bar{T}(v_{\text{gas}}, v_{\text{liquid}})$
 - \hookrightarrow expand in small $v_g - v_l$ to get $v_g - v_l \sim (T_c - \bar{T})^{1/2}$

② How does the volume change with pressure along the critical isotherm?

↪ at $T=T_c$, pressure is single-valued

$$\hookrightarrow \frac{\partial^2 p}{\partial v^2} = 0 \Rightarrow p - p_c \sim (v - v_c)^3$$

③ Define the compressibility $\kappa \equiv -\frac{1}{V} \frac{\partial V}{\partial P}|_T$. How does κ change as $T \rightarrow T_c$?

$$\hookrightarrow \text{at the critical point } \frac{\partial p}{\partial v}|_{T_c} = 0 \Rightarrow \frac{\partial p}{\partial v}|_{T, v_c} \sim T - T_c \\ \Rightarrow \kappa \sim (T - T_c)^{-1}$$

↪ so κ diverges as $T \rightarrow T_c$

• Experiments do not support these results, even though we only assumed analyticity:

$$\begin{aligned} \textcircled{1} \quad V_g - V_l &\sim (T - T_c)^\beta, \quad \beta \approx 0.32 \\ \textcircled{2} \quad p - p_c &\sim (v - v_c)^\delta, \quad \delta \approx 4.8 \\ \textcircled{3} \quad \kappa &\sim (T - T_c)^{-\gamma}, \quad \gamma \approx 1.2 \end{aligned} \quad \left. \begin{array}{l} \text{critical exponents} \end{array} \right\}$$

• These discrepancies arise from fluctuations

↪ in grand canonical, $\frac{\Delta N}{N} \sim \frac{1}{\sqrt{N}}$ ← density fluctuations diminish

$$\hookrightarrow \ln Z_{\text{grand}} = \beta p(T, m) V$$

$$\hookrightarrow N = \frac{1}{\beta} \frac{\partial}{\partial m} \ln Z_{\text{gr}} = V \frac{\partial p}{\partial m}|_{T, V} \quad \text{and} \quad \Delta N^2 = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial m}|_{T, V} \\ \Rightarrow \frac{\Delta N^2}{N} = \frac{1}{\sqrt{N}} \frac{\partial \langle N \rangle}{\partial p}|_{T, V}$$

$$\hookrightarrow \text{using the cyclic relation} \quad \frac{\Delta N^2}{N} = -\frac{1}{\beta} \left(\frac{\partial \langle N \rangle}{\partial V} \right)_{P, T} \cdot \underbrace{\frac{1}{\sqrt{N}} \frac{\partial V}{\partial p}}_{= -\kappa} |_{N, T}$$

↪ κ diverges as $T \rightarrow T_c$ so fluctuations become large.

The Ising Model

• Ising model: a d -dimensional lattice of N spins with $s_i = \pm 1$

• Two contributions to lattice energy:

1. Interactions of spins with magnetic field
2. Interactions of neighbouring spins

$$\Rightarrow E = -J \sum_{\langle ij \rangle} s_i s_j - B \sum_i s_i$$

↪ $\langle ij \rangle$ sums over the $q = 2d$ nearest neighbours

energy of configuration
↓

• If $J > 0$, spins prefer to be aligned (ferromagnetic)

• Work in canonical ensemble (N fixed) $\Rightarrow Z = \sum_{\text{config}} e^{-\beta E(s_i)}$
↪ magnetisation is the average spin: $m = \frac{1}{N} \sum_i \langle s_i \rangle = \frac{1}{N} \frac{\partial \ln Z}{\partial \beta}$

• The partition func can be approximated using mean field theory for small fluctuations:

$$\hookrightarrow s_i s_j = [(s_i - m) + m][(s_j - m) + m] = (s_i - m)(s_j - m) + m(s_i + s_j - 2m) + m^2$$

$$\hookrightarrow \text{neglect } (s_i - m)(s_j - m) \Rightarrow E_{\text{mf}} = -J \sum_{\langle ij \rangle} [m(s_i + s_j) - m^2] - B \sum_i s_i$$

↪ there are $\frac{Nq}{2}$ nearest neighbour pairs

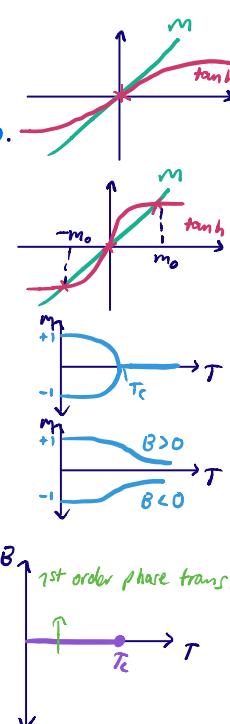
$$\Rightarrow E_{\text{mf}} = \frac{1}{2} J N q m^2 - (J q m + B) \sum_i s_i$$

↪ this is now just a 2-state system with $B_{\text{eff}} = B + J q m$

• With the MF approx, we have $Z = e^{-\frac{1}{k_B T} B_{\text{eff}} N q m^2} 2^N \cosh^N B_{\text{eff}}$

$$\hookrightarrow \text{can self-consistently solve for } m \Rightarrow m = \tanh(B_{\text{eff}} + \beta J q m)$$

- If $B=0$, $m = \tanh(\beta J q m) \rightarrow$ solve graphically
 - ↪ $\tanh(\beta J q m) \sim \beta J q m$ near the origin
 - ↪ for $\beta J q < 1$ (high temp), the only solution is $m=0$. Thermal fluctuations dominate.
 - ↪ if $\beta J q > 1$, there are 3 solutions. $m=0$ is unstable, but $m = \pm m_0$ are stable
 - ↪ at some $T=T_c$ given by $\beta J q = 1$, there is a discontinuous change in magnetisation
- For $B \neq 0$, magnetisation $\rightarrow 0$ smoothly as $T \rightarrow \infty$
 - ↪ at low temperatures, the only stable solution has $m = \text{sign}(B)$ (other 2 are unstable)
 - ↪ m changes discontinuously if we vary B , so there is a phase boundary on the $B-T$ plane



Critical exponents

- ① How does m vary as $T \rightarrow T_c$ from below ($B=0$)?
 - ↪ Taylor expansion of $\tanh \Rightarrow m \propto \beta J q m - \frac{1}{3} (\beta J q m)^3 + \dots$
 - ↪ $m_0 \sim \pm (T_c - T)^{1/2}$ → turns off abruptly when $T=T_c$
 - ↪ analogous to $v_g - v_l \sim (T_c - T)^{1/2}$ for liquid-gas vdW
- ② How does m vary with B at $T=T_c$
 - ↪ $\beta J q = 1 \Rightarrow m = \tanh\left(\frac{B}{Jq} + m\right) \approx m + \frac{B}{Jq} - \frac{1}{3}\left(m + \frac{B}{Jq}\right)^3 + \dots$
 - ↪ $m \propto B^{1/3}$, analogous to $(v - v_c) \sim (P - P_c)^{1/3}$ from vdW

- ③ How does the susceptibility $\chi = N \left(\frac{\partial m}{\partial B} \right)_T$ vary as $T \rightarrow T_c$ from above ($B=0$)?

$$\hookrightarrow \chi = \frac{N B}{\cosh^2(\beta J q m)} \left(1 + \frac{J q}{N} \chi \right)$$

$$\hookrightarrow T \rightarrow T_c \Rightarrow m \rightarrow 0 \therefore \chi = \frac{N B}{1 - J q \beta} \sim (T - T_c)^{-1}$$

↪ χ diverges, similar to compressibility

- For $d=1$, MFT is completely wrong (no phase transition)
- For $d > 2$, MFT is qualitatively correct but quantitatively wrong.
 - ↪ e.g. for $d=2$ $m_0 \sim (T_c - T)^{\beta}$, $\beta = 1/8$
 - ↪ $m \sim B^{1/8}$, $\delta = 15$
 - ↪ $\chi \sim (T - T_c)^{-\gamma}$, $\gamma = 3/4$
- For $d=3$ measured values of critical exponents are the same as for the liquid-gas system.
- For $d > 4$, MFT is very nearly correct.

Landau theory

- Landau theory is a unified way of understanding phase transitions (applies to all systems).

- MF approx for Ising: $Z = e^{-\frac{1}{2} \beta J q N m^2} 2^N \cosh(\beta B_{\text{eff}})$

$$\hookrightarrow F = -\frac{1}{\beta} \ln Z = \frac{1}{2} J N q m^2 - \frac{N}{\beta} \ln[2 \cosh(\beta B_{\text{eff}})]$$

Ⓐ ↳ Landau theory considers $F(m)$ without finding the correct self-consistent value of m .

↳ equilibrium config: $\frac{\partial F}{\partial m} = 0 \Rightarrow m = \tanh(\beta B_{\text{eff}})$ agrees with previous result

- In Landau theory, m is an order parameter ($m \neq 0$ ordered, $m = 0$ random)

↳ For general systems, the order parameter should be finite below T_c but vanishes above T_c

↳ e.g. for liquid-gas system, use $m = V_{\text{gas}} - V_{\text{liquid}}$

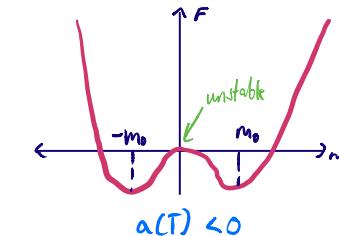
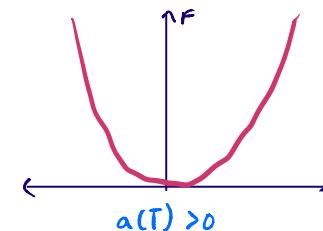
↳ we can then expand the free energy in the vicinity of T_c , where m is small.

- Assume the free energy is symmetric in m (as in Ising with $B=0$)

↳ expansion: $F(T; m) = F_0(T) + \alpha(T)m^2 + b(T)m^4 + \dots$

↳ assume $b(T) > 0$ (such that $F \uparrow$ for large m), so equilibrium behaviour depends on the sign of $\alpha(T)$

↳ $\alpha(T_c) \equiv 0$, so as T decreases, we go from $\alpha(T) > 0 \rightarrow \alpha(T) < 0$



↳ can be shown that this is a 2nd order phase transition

- Typically $\alpha(T) \propto \alpha_0(T-T_c)$ and $b(T)=b_0$

↳ $\frac{\partial F}{\partial m} = 0 \Rightarrow m_0 = \sqrt{\frac{\alpha_0}{2b_0}} (T_c - T)^{1/2}$ for $T < T_c$

↳ this reproduces the critical exponent of the Ising/vdW systems

1st order phase transition

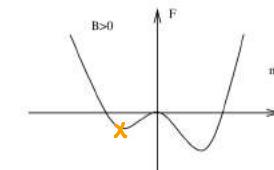
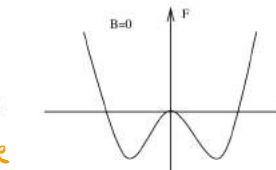
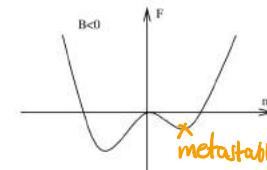
- Now we allow asymmetry in m , e.g. $B \neq 0$ Ising model.

$$F(T; m) = F_0(T) + \alpha(T)m + \alpha(T)m^2 + \gamma(T)m^3 + b(T)m^4 + \dots$$

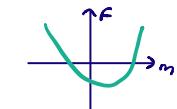
↳ as before, assume $b(T) > 0$

↳ as B changes from +ve to -ve, α and γ change sign

↳ for low temperatures, a nonzero field results in 2 stable equilibria



- At high temperatures, the metastable equilibrium disappears at the spinodal point



Landau-Ginzberg theory

- Corrects Landau theory by including fluctuations in the order param.

↳ order param becomes $m(r)$

↳ free energy now has a 'stiffness' that resists changing m

↳ free energy is now a functional, e.g. in symmetric case:

$$F[m(r)] = \int d^d r [a(t)m^2 + b(t)m^4 + c(t)(\nabla m)^2 + \dots]$$

- Minimise using the calculus of variations

↳ $m(r) \rightarrow m(r) + \delta m(r)$

$$\begin{aligned} \delta F &= \int d^d r [2a m \delta m + 4b m^3 \delta m + 2c (\nabla m) \cdot \nabla \delta m + \dots] \\ &= \int d^d r [2am + 4bm^3 - 2c \nabla^2 m + \dots] \delta m \end{aligned}$$

$$\delta F = 0 \Rightarrow c \nabla^2 m = am + 2bm^3$$

↳ $m = \text{const}$ recovers Landau theory

↳ in 1D, Landau-Ginzberg theory describes domain walls.