Pensum based on Lecture notes (F. Ravndal)

Module I: Equilibrium statistical ensemble (Ch. 1.1-1.8, 3.1-3.6)
Module II: Non-interacting particles (Ch. 2.1-2.5)
Module III: Weakly interacting particles (Ch. 4.1-4.3)
Module IV: Ideal quantum gases (5.1-5.7)
Module V: Magnetism (6.1-6.6)
Module VI: Stochastic and non-equilibrium processes (7.1-7.3; 8.1-8.2)

Final exam: 04. June 2019, 14:30 (4 hours)
Sal 3B Silurveien 2

Allowed material at the exam:

- Electronic calculator
- K. Rottman: Matematisk formelsamling
- Øgrim and Lian or Angell and Lian: Fysiske størrelser og enheter
- One A4 sheet of notes (both sides can be used)

Module I: Equilibrium statistical ensemble

- Thermodynamics laws
- Thermodynamic potentials and Legendre transforms
- Response functions and Maxwell's relations
- Liouville's theorem
- Microcanonical ensemble
- Canonical ensemble
- Grand-canonical ensemble

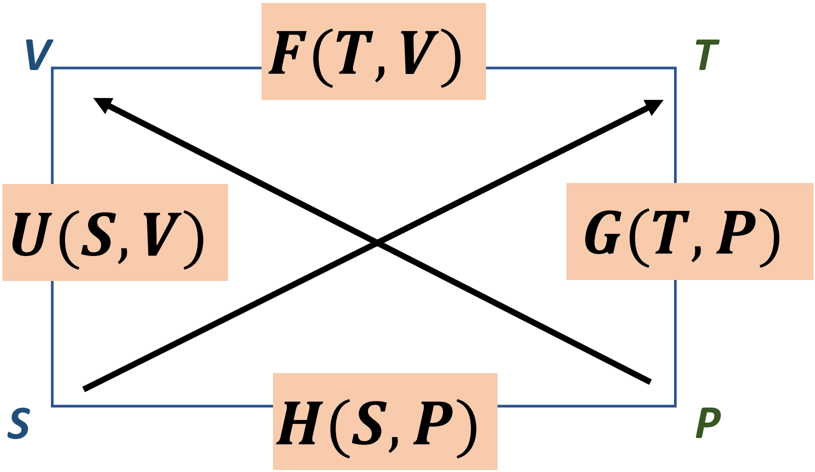
Thermodynamic potential and Legendre transforms

Thermodynamic Potentials	Thermodynamic (natural) Variables
U (S,V,N)	S, V, N
H (S,P,N)	S, P, N
F (T,V,N)	V, T, N
G (T,P,N)	P, T, N

$$dU = TdS - PdV + \mu dN, \qquad U(T,V,N) = ST - PV + \mu N$$
$$dH = TdS + VdP + \mu dN, \qquad H(S,P,N) = U(S,V,N) + PV$$
$$dF = -SdT - PdV + \mu dN, \qquad F(T,V,N) = U(S,V,N) - TS$$
$$dG = -SdT + VdP + \mu dN, \qquad G(T,P,N) = U(S,V,N) - TS + PV$$

Extensive variables

Intensive variables



$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P, \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \qquad K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

Liouville's theorem

- Ensemble density $\rho(p,q)$ is the number of systems that occupy a microstate per unit phase space volume
- $\rho(p,q)d\omega$ is the probability of finding the systems in a given microstate between (p,q) and $(pdp, q + d\rho)$

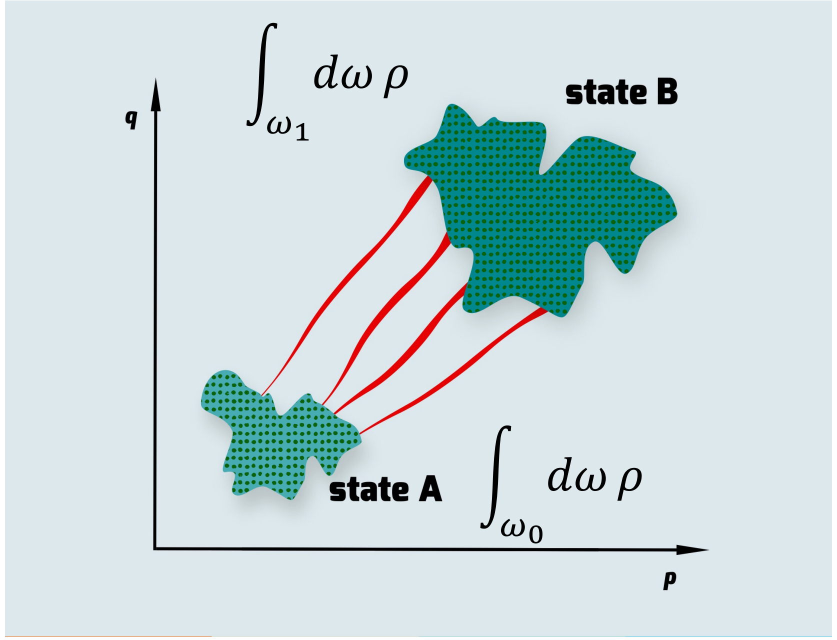
$$\int \rho(p,q)d\omega = 1$$

- Liouville's theorem: Ensemble density is conserved

$$\frac{\partial\rho}{\partial t} + \{\rho, H\} = 0$$

- For equilibrium systems $\{\rho, H\} = 0$, *with a general solution*

$$\rho = \rho(H)$$



$$\boldsymbol{d\omega \equiv \frac{d^{3N}p\,d^{3N}q}{(2\pi\hbar)^{3N}}}$$

Microcanonical ensemble (isolated systems)

- Equilibrium ensemble density

$$\rho(p,q) = \frac{1}{\Sigma}\delta(H(p,q) - E),$$

- Microcanonical density of states: phase space area over all microstate with a fixed energy E

$$\Sigma(E,V,N) = \int d\omega\, \delta(H(p,q) - E)$$

- Microcanonical phase space volume

$$\Omega(E,V,N) = \int_{H(p,q)\leq U} d\omega = \int_0^E dE'\, \Sigma(E')$$

Thermodynamics of microcanonical ensemble

Boltzmann Entropy

$$S(U,V,N) = k \ln \Omega\,(U,V,N)$$

Temperature $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$

Pressure $\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$

Chemical potential $\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}$

Helmholtz free energy $F = U - TS = U - kT \ln \Omega$

Ideal gas in the microcanonical ensemble

- Phase space volume

$$\Omega(E) = \frac{\mathrm{V}^N}{(2\pi\hbar)^{3N}} \frac{\pi^{\frac{3N}{2}}}{(3N/2)!} (2mE)^{\frac{3N}{2}}$$

- *Density of states* $\Sigma(E) = \frac{\partial\Omega}{\partial E}$

- *Entropy*

$$S(E,V,N) = kN\left\{\frac{5}{2} + \log\frac{V}{N}\left(\frac{mE}{3\pi N\hbar^2}\right)^{\frac{3}{2}}\right\}$$

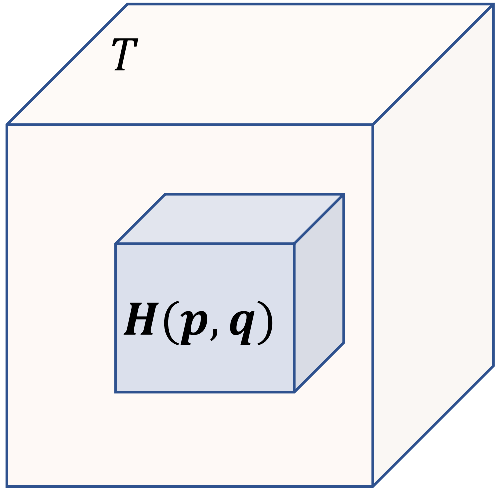
- *Temperature*

$$\frac{1}{T} = \frac{\partial S}{\partial E} = kN\,\frac{\partial}{\partial E}\log E^{\frac{3}{2}} = \frac{3Nk}{2}\frac{1}{E} \rightarrow E = \frac{3}{2}NkT$$

- *Pressure*

$$\frac{P}{T} = \frac{\partial S}{\partial V} = \frac{Nk}{V} \rightarrow PV = NkT$$

Canonical ensemble (systems in a thermal bath)



- Equilibrium ensemble density $\rho(p,q) = \frac{1}{Z} e^{-\beta H(p,q)}$
- Canonical partition function $\mathrm{Z(T,V,N)} = \int d\omega e^{-\beta H(p,q)}$

$$Z = \int dE\, e^{-\beta E} \Sigma(E)$$

$$Z = e^{-\beta F}$$

- Probability of a macrostate with energy E, $P(E) = \frac{\Sigma(E)}{Z}\, e^{-\beta E}$
  - Average energy $\langle \boldsymbol{E} \rangle = -\frac{\boldsymbol{\partial}}{\boldsymbol{\partial\beta}}\, \boldsymbol{log\, Z(T)}$
  - Fluctuations around the average energy $\langle \boldsymbol{\Delta E^2} \rangle = \frac{\boldsymbol{\partial^2}}{\boldsymbol{\partial\beta^2}} \mathbf{log}\, \boldsymbol{Z(T)}$

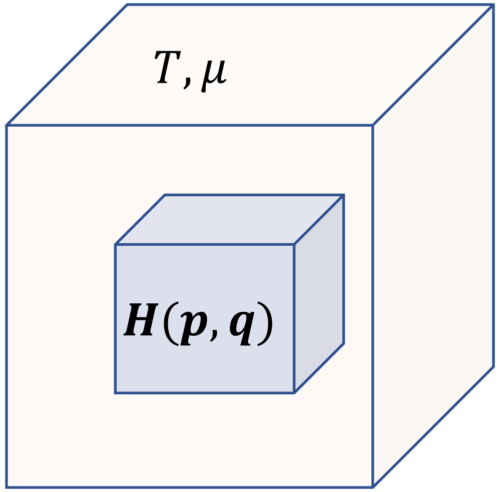
Ideal gas in the canonical ensemble

- $Z_1(T,V) = \frac{V}{h}\int d^3p\, e^{-\frac{\beta p^2}{2m}} = \frac{V}{\Lambda^3}$, where $\Lambda = \frac{1}{\sqrt{2m\pi kT}}$ is the thermal wavelength
- Gas of indistinguishable particles:

$$Z(T,V,N) = \frac{Z_1^N}{N!} = \frac{V^N}{N!\,\Lambda^{3N}} == e^{-\beta F(T,V,N)}$$

- $S = -\left(\frac{\partial F}{\partial T}\right)_V = Nk\log\frac{V}{N}$
- $P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{NkT}{V}$

Grand canonical ensemble (system in a thermal and particle reservoir)



- **Equilibrium ensemble density**

$$\rho(p,q,n) = \frac{1}{\Xi}\frac{1}{n!}e^{\beta(\mu n - H(p,q))}$$

- ***Grand-canonical partition function***

$$\Xi(T,\mu) = \sum_{n=0}^{\infty}\frac{e^{\beta\mu n}}{n!}Z(T,n)$$

$$\Xi(T,\mu) = \sum_{n=0}^{\infty}e^{\beta\mu n}Z_n(T)$$

$$\Xi(T,\mu) = e^{-\beta\Omega}$$

- **Distribution of particle number in a macrostate** $P(N) = \frac{Z(T,N)}{\Xi}e^{\beta\mu N}$

Ideal gas in the grand-canonical ensemble

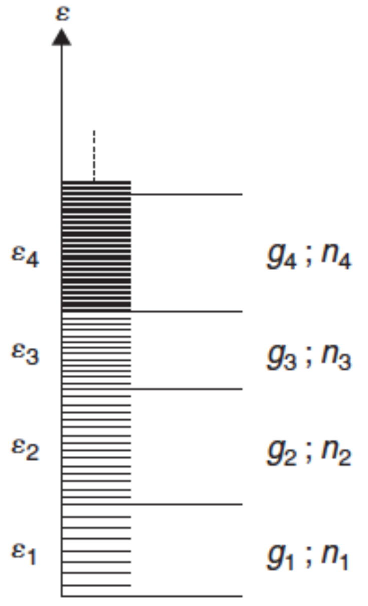
- $\Xi(T,V,\mu) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,V,N)$
- $\Xi(T,V,\mu) = \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{V}{\Lambda^3} e^{\beta\mu}\right)^N = e^{zV}, \text{where } \mathrm{z} = \frac{\mathrm{e}^{\beta\mu}}{\Lambda^3}\ \textit{is called fugacity}$

- $\Xi(T,V,\mu) = e^{zV} = e^{-\beta\Omega}$
- Landau free energy $\Omega = -kTV \frac{e^{\beta\mu}}{\Lambda^3(T)}$
- $\langle \mathrm{N} \rangle = \frac{\partial \Omega}{\partial \mu} = V \frac{e^{\beta\mu}}{\Lambda^3(T)} = \mathrm{zV} \rightarrow \Omega = -\mathrm{kT}\langle N \rangle$
- $P = -\frac{\partial \Omega}{\partial V} = kTz \rightarrow P = \frac{\langle N \rangle kT}{V}$

Module II: Non-interacting particles

- Boltzmann statistics
- Bose-Einstein distribution
- Fermi-Dirac distribution

Maxwell-Boltzmann: free particles



- Equilibrium distribution of particles in an energy state

$$n_i = \frac{N}{Z_1} e^{-\beta\epsilon_i} = e^{-\beta(\epsilon_i-\mu)}, \quad Z_1 = \sum_i e^{-\beta\epsilon_i}, \quad N = Z_1 e^{\beta\mu}$$

- Probability of a specific microstate at fixed T and μ in the equilibrium

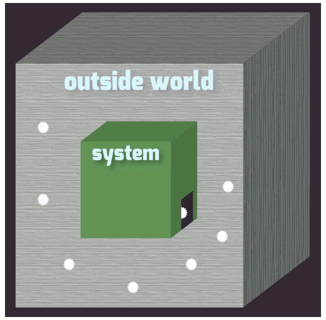
$$P(s) = \frac{1}{\Xi(T,\mu)} \frac{1}{N_s!} e^{-\beta(E_s-\mu N_s)}, \qquad N_s = \sum_i n_i, \qquad E_s = \sum_i \epsilon_i n_i$$

- Grand-canonical partition function (sum over particle numbers and sum over all the energy states for each individual particle)

$$\Xi(T,\mu) = \sum_{N_s} \frac{1}{N_s!} \sum_{E_s} e^{-\beta(E_s-\mu N_s)} = \sum_{N_s} \frac{1}{N_s!} \prod_{k=1}^{N_s} \sum_{\epsilon_k} e^{-\beta(\epsilon_k-\mu)}$$

$$\Xi(T,\mu) = \sum_{N_s} \frac{1}{N_s!} \left(\lambda \sum_i e^{-\beta\epsilon_i}\right)^{N_s} = e^{\lambda Z_1}, \qquad \lambda = e^{\beta\mu}, \qquad Z_1 = \sum_i e^{-\beta\epsilon_i}$$

Maxwell-Boltzmann: free particles



- Probability of having N_s particles in a <u>macroscopic</u> state at T and μ

$$P(N_s) = \frac{1}{\Xi(T,\mu)} \frac{1}{N_s!} \sum_{\boldsymbol{E_s}} e^{-\beta(E_s - \mu N_s)} = \frac{1}{N_s!} (Z_1\lambda)^{N_s} e^{-Z_1\lambda}$$

$$P(N_s, N) = \frac{1}{N_s!} N^{N_s} e^{-N}, \qquad \langle N_s \rangle = N(T,\mu) = Z_1(T)\lambda(T,\mu)$$

Total number of particles in a macrostate is a fluctuating (random)quantity drawn from a *Poisson distribution with* $\langle N_s \rangle = N$ *as the average number*

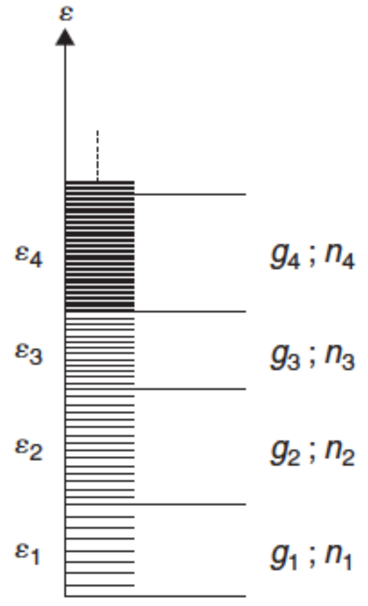
- $\langle \Delta N_s^2 \rangle = \langle N_s^2 \rangle - \langle N_s \rangle^2 = \langle N_s \rangle$
- ***Relative number fluctuations*** $\frac{\langle \Delta N_s^2 \rangle}{\langle N_s \rangle^2} = \frac{1}{N} = \frac{1}{Z_1\lambda} \ll 1$

Maxwell-Boltzmann: free particles

- Probability for an occupation number n in ϵ_i energy state

$$P_i(n) = \frac{\frac{1}{n!}\left(\lambda e^{-\beta\epsilon_i}\right)^n}{\left(\sum_n \frac{1}{n!}(\lambda e^{-\beta\epsilon_i})^n\right)} = \frac{1}{n!}\frac{\left(\lambda e^{-\beta\epsilon_i}\right)^n}{\exp(\lambda e^{-\beta\epsilon_i})}$$

$$P_i(n, n_i) = \frac{1}{n!}n_i^n e^{-n_i}, \qquad n_i = \langle n\rangle_i = \lambda e^{-\beta\epsilon_i}$$



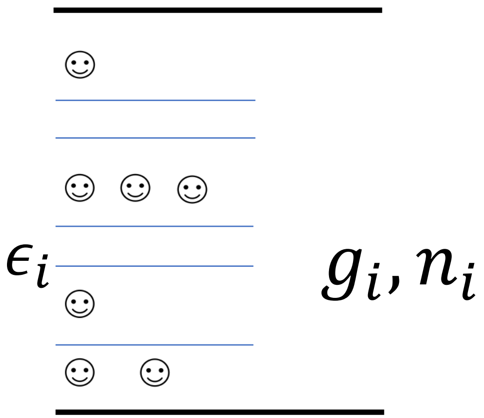
Occupation number of an energy state is also a random number following *Poisson distribution with* $n_i = \lambda e^{-\beta\epsilon_i}$

- $\langle \Delta n^2\rangle_i = \langle n^2\rangle_i - {\langle n\rangle_i}^2 = n_i$
- ***Relative number fluctuations*** $\frac{\langle \Delta n^2\rangle_i}{n_i^2} = \frac{1}{n_i} = \frac{Z_1 e^{\beta\epsilon_i}}{N} \ll 1$

Bose-Einstein statistics:

- Equilibrium (average) occupation number for an energy state

$$\langle \boldsymbol{n_i} \rangle = \frac{\mathbf{1}}{\boldsymbol{e^{\beta(\epsilon_i-\mu)}} - \mathbf{1}} = \frac{\mathbf{1}}{\boldsymbol{e^{\beta\epsilon_i}\lambda^{-1}} - \mathbf{1}}$$

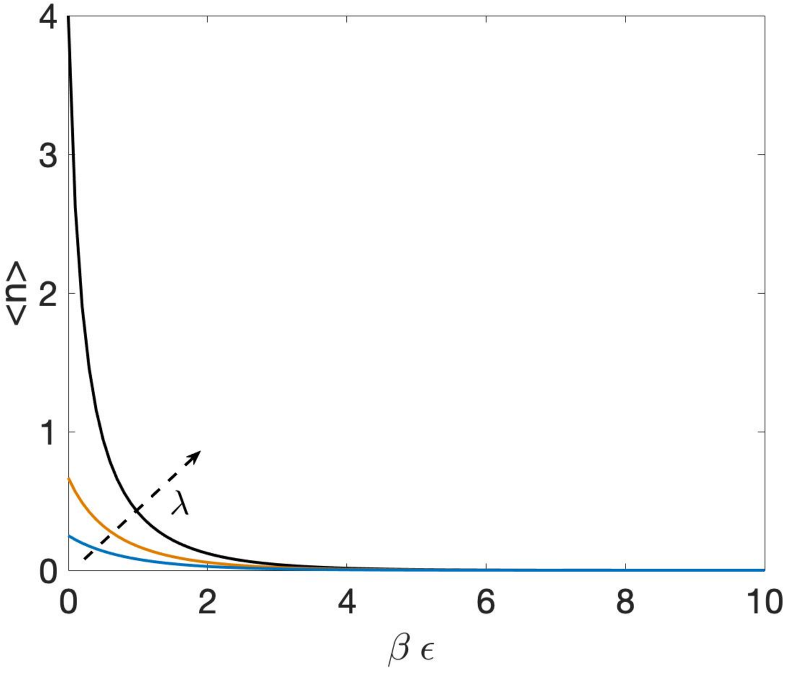


- Probability of a specific microstate at fixed T and μ in the equilibrium

$$\boldsymbol{P(s)} = \frac{\mathbf{1}}{\boldsymbol{\Xi(T,\mu)}} \boldsymbol{e^{-\beta(E_s-\mu N_s)}}, \qquad N_s = \sum_i n_i\,, \qquad E_s = \sum_i \epsilon_i n_i$$

- Grand-canonical partition function

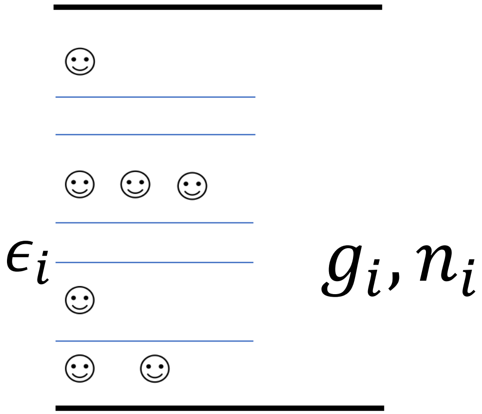
$$\Xi^{(BE)}(T,\mu) = \prod_i \left(\sum_{n_i=0}^{\infty} \left(\lambda e^{-\beta\epsilon_i}\right)^{n_i} \right) = \prod_i \left(\frac{1}{1-\lambda e^{-\beta\epsilon_i}} \right)$$



Bose-Einstein statistics:

- Probability for having n bosons in a given energy state

$$P_i^{(BE)}(n) = \left(1 - \lambda e^{-\beta\epsilon_i}\right)\left(\lambda e^{-\beta\epsilon_i}\right)^n = \frac{1}{\langle n_i\rangle + 1}\left(\frac{\langle n_i\rangle}{\langle n_i\rangle + 1}\right)^n$$



geometric distribution: probability that a particle occupies an energy state is independent of the number of particles already in that states --- tendency of «bunching» together

$$\langle n^2\rangle_i = \sum_{n=0}^{\infty} n^2 \frac{1}{\langle n_i\rangle + 1}\left(\frac{\langle n_i\rangle}{\langle n_i\rangle + 1}\right)^n$$

$$\langle n^2\rangle_i = \frac{1}{\langle n_i\rangle + 1}\left(x\frac{d}{dx}\right)^2 \sum_{n=0}^{\infty} x^n$$

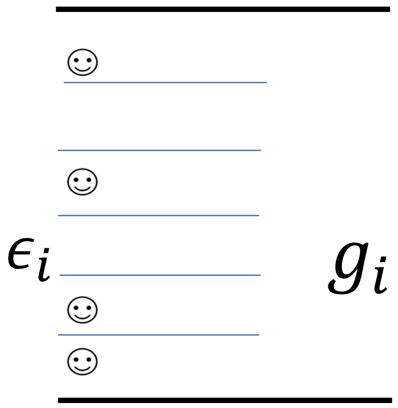
$$\langle n^2\rangle_i = \frac{1}{\langle n_i\rangle + 1}\left(x\frac{d}{dx}\right)^2 \left(\frac{1}{1-x}\right), \qquad x = \frac{\langle n_i\rangle}{\langle n_i\rangle + 1}$$

$$\langle n^2\rangle_i = \langle n_i\rangle + 2\langle n_i\rangle^2$$

Relative number fluctuations $\dfrac{\langle \Delta n^2\rangle_i}{n_i^2} = \dfrac{1}{n_i} + 1$

Increased number fluctuations relative to be MB statistics

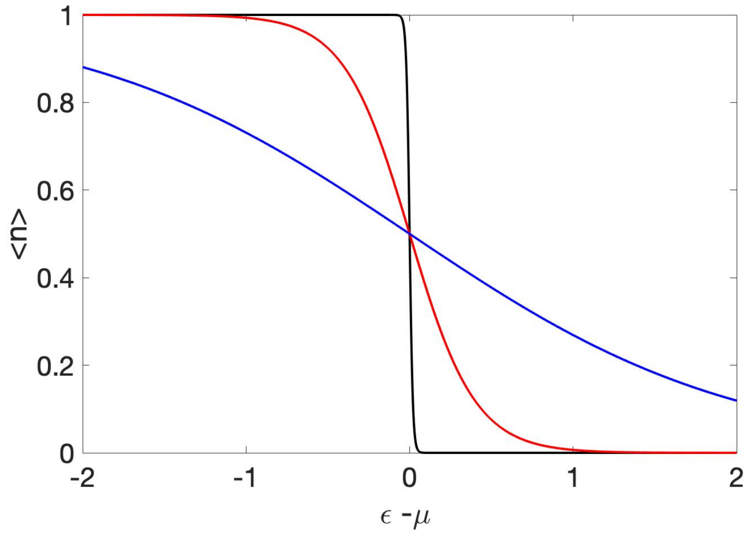
Fermi-Dirac statistics



$$g_i > n_i$$

Equilibrium occupation number for an energy state

$$\boldsymbol{n_i = \frac{1}{e^{\beta(\epsilon_i-\mu)}+1} = \frac{1}{e^{\beta\epsilon_i}\lambda^{-1}+1}}$$



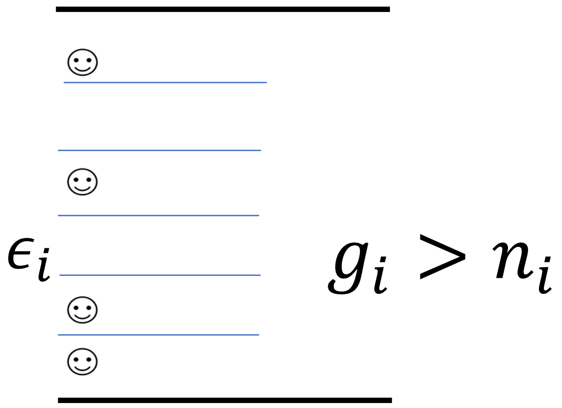
- Probability of a specific microstate at fixed T and μ in the equilibrium

$$\boldsymbol{P(s) = \frac{1}{\Xi(T,\mu)} e^{-\beta(E_s-\mu N_s)}}, \qquad N_s = \sum_i n_i\,, \qquad E_s = \sum_i \epsilon_i n_i$$

- **Grand-canonical partition function**

$$\Xi(T,\mu) = \prod_i \left(\sum_{n_i} e^{-\beta n_i(\epsilon_1-\mu)}\right) = \prod_i \left(1+e^{-\beta(\epsilon_i-\mu)}\right)$$

Free fermions: Fermi-Dirac statistics



- **Probability for having n free fermions in a given energy state ϵ_i at fixed T and μ is the same as the average occupation number n_i**

$$P_i^{(FD)}(n) = \frac{\left(\lambda e^{-\beta\epsilon_i}\right)^n}{1+\lambda e^{-\beta\epsilon_i}} = \begin{cases} 1-n_i, & n=0 \\ n_i, & n=1 \end{cases}$$

- $\langle n^2\rangle_i = \sum_{i=0}^{1} n^2 P_i(n) = P_i(1) = n_i$

- Relative mean square fluctuations: as the occupation probability increases, fluctuations are suppressed

$$\frac{\langle \Delta n^2\rangle_i}{n_i^2} = \frac{1}{n_i} - 1 \rightarrow 0, as\ n_i \rightarrow 1$$

- *Negative statistical correlation– statistical repelling force*

Classical limit: $\epsilon_i \ll kT, \mu(T) \ll 0$ (high-T limit)

- Fermi Dirac/Bose-Einstein distribution:

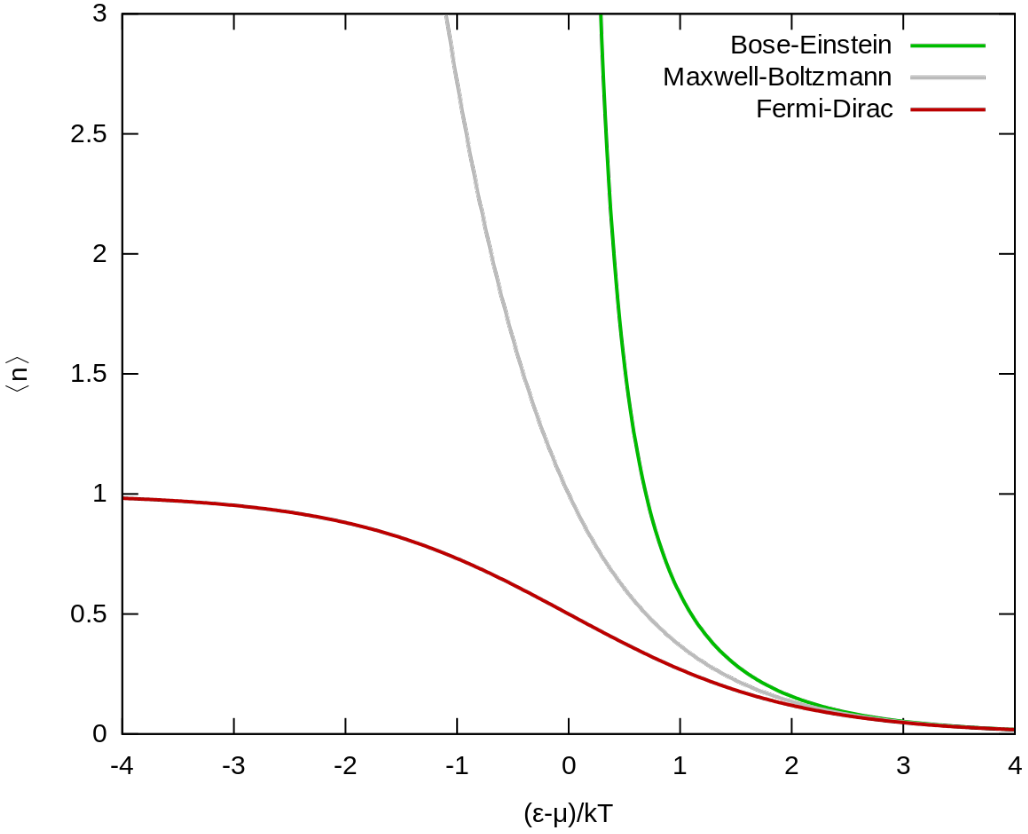
$$n_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1} = e^{\beta\mu} \frac{e^{-\beta\epsilon_i}}{1 \pm e^{-\beta\epsilon_i} e^{\beta\mu}} \approx e^{\beta\mu} e^{-\beta\epsilon_i}$$

- Maxwell Boltzmann distribution:

$$n_i^{MB} = \frac{N}{Z_1} e^{-\beta\epsilon_i} = e^{\beta\mu} e^{-\beta\epsilon_i}$$

- Classical ideal gas limit: $\mu = -kT \ln \frac{V}{N\Lambda^3(T)} \ll 0 \rightarrow$

$$\boldsymbol{T \gg T^* = \left(\frac{h^2}{2\pi m k}\right)\rho^2, \qquad \rho = \frac{N}{V}}$$



Module III: Weakly interacting particles: classical fluids

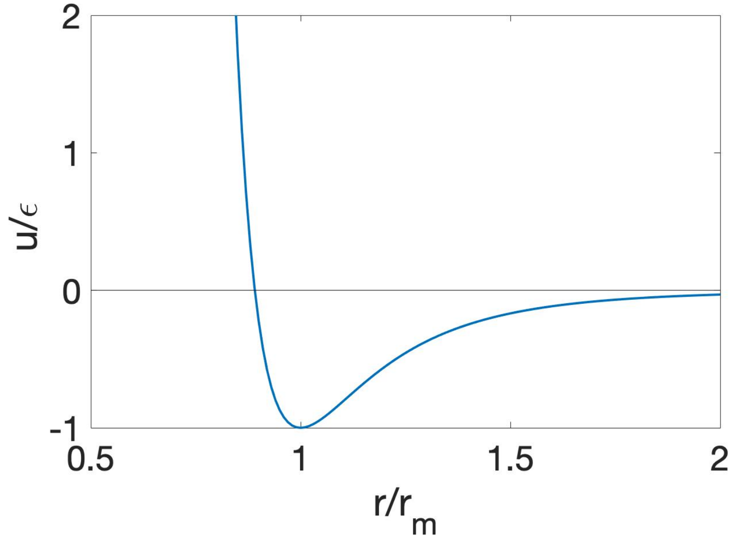
- Virial theorem
- Mean-field theory and van der Waals fluids
- Phase transitions in the van der Waals systems

Classical gases and liquids

- Statistical mechanics of *weakly-interacting* classical *indistinguishable* particles
- Translational and rotational symmetric Hamiltonian H_N

$$H_N(p,q) = \sum_{j=1}^{3N} \frac{p_j^2}{2m} + U(q_1, q_2, \cdots q_{3N})$$

$$H_N = \sum_{i=1}^{N} \frac{|\vec{p}_i|^2}{2m} + \frac{1}{2}\sum_{j\neq i} u(r_{ij}), \qquad r_{ij} = |\vec{r}_i - \vec{r}_j|, \qquad \vec{r} = (x,y,z), \qquad \vec{p} = (p_x, p_y, p_z)$$

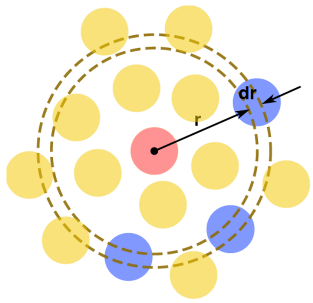


- Homogeneous and isotropic matter: gases and liquids
- $Z_N(T,N) = \frac{1}{N!}\int d\omega\, e^{-\beta H_N(p,q)} = \frac{1}{N!}\frac{Q_N}{\Lambda^{3N}}$
- $Q_N = \int d^N\vec{r}\, e^{-\beta U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)}$

configurational partition function: contains all the information about the particle positions

Correlation functions

Mean density of particles is uniform for a *translational and isotropic system*



$$\langle n(\vec{r})\rangle = \left\langle \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i) \right\rangle = \rho = \frac{N}{V}$$

Density correlation of pairs of particles separated by $\vec{r}-\vec{r}'$

$$\langle n(\vec{r})n(\vec{r}')\rangle = \left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \delta(\vec{r}-\vec{r}_i)\,\delta\left(\vec{r}'-\vec{r}_j\right) \right\rangle \equiv G(\vec{r}-\vec{r}')$$

$$G(\vec{r}-\vec{r}') = \rho^2 g(\vec{r}-\vec{r}') + \rho\delta(\vec{r}-\vec{r}'),$$

$$\rho^2 g(\vec{r}-\vec{r}') \equiv \rho^2 g(|\vec{r}-\vec{r}'|) = \rho^2 g(r)$$

Average properties

Average energy

$$\langle E\rangle = \frac{3N}{2}kT + \frac{\rho N}{2}\int d\vec{r}\, u(r)g(r)$$

Particle number fluctuations

$$\langle \Delta N^2\rangle = \langle N\rangle + \langle N\rangle\rho\int d\vec{r}\,[g(r)-1]$$

Virial theorem

$$2\langle K\rangle = -\left\langle \sum_k \vec{r}_k\cdot\vec{F}_k\right\rangle \rightarrow 3NkT = \frac{N\rho}{2}\int d\vec{r} r^2\, u'(r)\, g(r) + 3PV$$

$$P = \rho\left[kT - \frac{\rho}{6}\int d\vec{r}\, r\, u'(r)g(r)\right]$$

Mean-field approximation: van der Waals system

In the mean field approximation, we assume that all particles experience the same effective potential field

$$U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \sum_i \sum_{i \neq j} u(r_{ij}) = \sum_{i=1}^{N} \overline{u} = N\overline{u}$$

Self-consistent equation

$$\overline{u} = \frac{\langle U_N \rangle}{N} = \frac{\rho}{2} \int d\vec{r}\, u(r) g(r) = -\frac{Na}{V}, \qquad a > 0$$

Canonical partition function

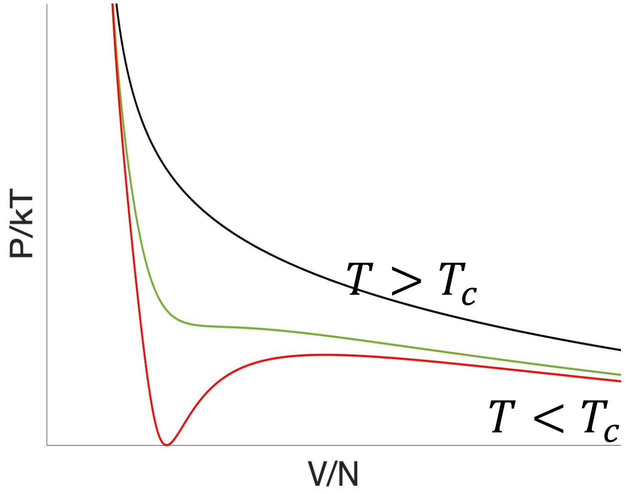
$$Z_N = \frac{1}{N!} \frac{Q_N}{\Lambda^{3N}}, \qquad Q_N = (V - Nb)^N e^{-N\beta\overline{u}}$$

Helmholtz free energy $F_N = -kT \ln(Z_N)$

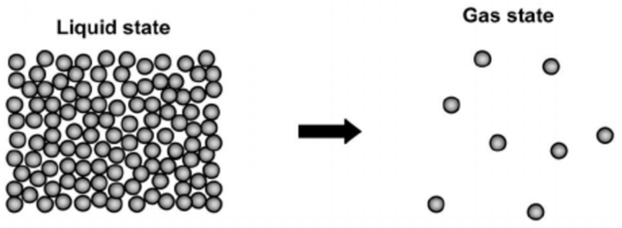
$$F_N = -NkT \left[\ln\left(\frac{V}{N\Lambda^3(T)} \right) + 1 \right] - NkT \ln\left(1 - \frac{Nb}{V} \right) - \frac{N^2 a}{V}$$

Equation of state

$$P = kT \left(\frac{N}{V - Nb} - \frac{a}{kT} \frac{N^2}{V^2} \right)$$



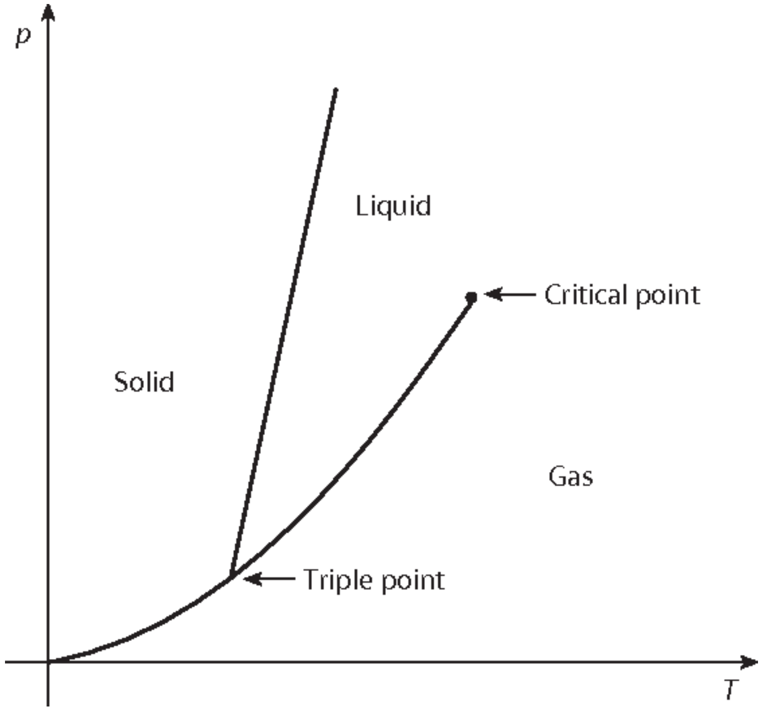
Liquid-gas phase transitions



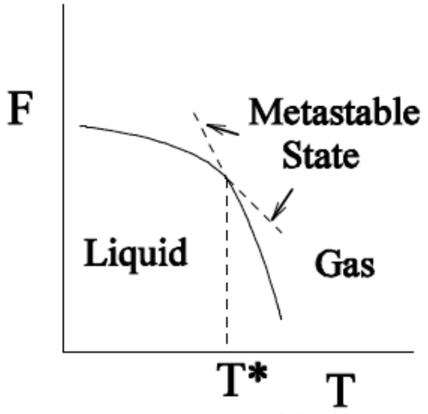
- Van der Waals equation of state for fluids

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

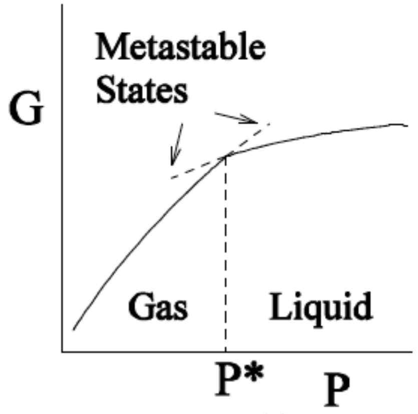
- Abrupt phase transition is represented by the phase coexistance boundary $P_{\text{lg}}\ \ (T_{\text{lg}}\ \ )$ in the P-T phase diagram
  - **First** order derivaties of the thermodynamic potential are discontinuous: entropy and volume
  - **Clausius Clapeyron relation:** How the pressure depends on the temperature on the vaporisation/condensation phase boundary
  - Phase transition from liquid to vapor at a constant Gibbs free energy $G(P, T, N)$
- There is a ***unique*** **critical point ($\mathbf{T_c}, \boldsymbol{P_c}, \boldsymbol{V_c}$)** at which the phase transition turns **critical**
  - First order derivaties of the thermodynamic potential are *continuous, but the second* order derivaties, like heat capacity, susceptibility, are *power-law divergent neat the critical point*
  - *Critical phase transitions* are robust to microscopic details and exhibit *universal scaling* properties, e.g. **critical scaling exponents**



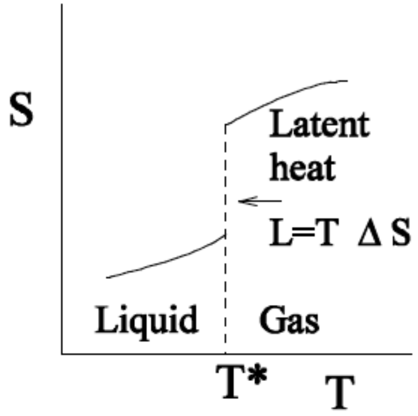
Abrupt phase transition



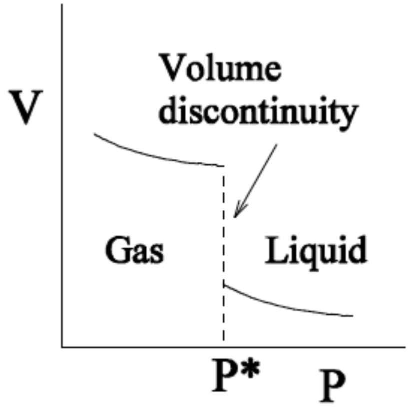
(a)



(c)



(b) $S = -(\partial F/\partial T)_P$



(d) $V = (\partial G/\partial P)_T$

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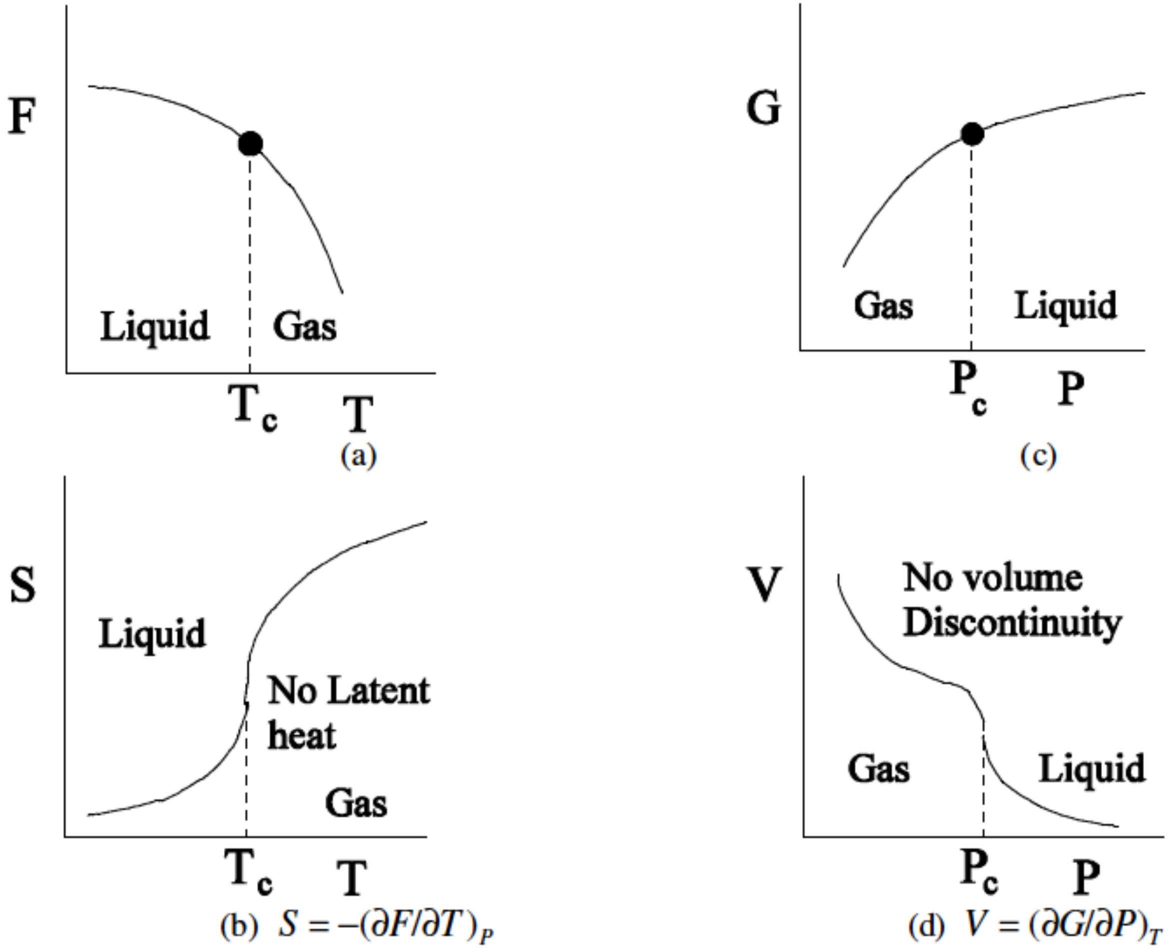
Critical phase transition



(a)

(c)

(b) $S = -(\partial F/\partial T)_P$

(d) $V = (\partial G/\partial P)_T$

http://www.iitg.ac.in/santra/course_files/ph704/critical_ph.pdf

Module IV: Ideal quantum gases

- Blackbody radiation: Photon gas
- Debye model: phonon gas
- Ideal Bose gas: Bose Einstein condensation
- Ideal Fermi gas: Degenerate Fermi gases

Ideal quantum gas

Consider a system of $N = \sum_j n_j$ fre. quantum particles with number n_j of particles in each energy state ϵ_j

Fermions: $n_j = 0,1$

Bosons: $n_j = 0,1,2,\cdots$

Grand-canonical partition function:

Unconditioned sum weighted by the Gibbs factor over all microstates with $\{n_j\}$ partition of particles between the energy levels $\{\epsilon_j\}$,

$$\Xi = \sum_{\{n_j\}} e^{-\beta \sum_j (\epsilon_j - \mu) n_j} = \prod_j \sum_{n_j} e^{-\beta(\epsilon_j - \mu) n_j}$$

Grand-canonical partition function:

$$\Xi = \prod_j \left(\frac{1}{1 \pm e^{-\beta\left(\epsilon_j - \mu\right)}}\right)^{\mp 1}, \begin{cases} top\ sign:\ fermions \\ bottom\ sign:\ bosons \end{cases}$$

Landau free energy: $\Omega(\mathrm{T}, \mathrm{V}, \mu) = -PV = -kT \log \Xi$

$$\Omega = \mp kT \sum_j \log\left[1 \pm e^{-\beta(\epsilon_j - \mu)}\right]$$

Thermodynamics of ideal quantum gases

Pressure $P(T,\mu)$

$$PV = \pm kT \int d\epsilon D(\epsilon) \log\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) \qquad (1)$$

Equation for the average number of particles provides the relationship between the density ρ *and chemical potential* μ*:*

$$\langle N\rangle(T,V,\mu) = \int d\epsilon D(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} \pm 1} = \int d\epsilon\, D(\epsilon) \langle n\rangle_\epsilon \qquad (2)$$

Average energy:

$$\langle E\rangle(T,V,\mu) = \int d\epsilon D(\epsilon) \frac{\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1} = \int d\epsilon\, D(\epsilon) \langle n\rangle_\epsilon \epsilon \qquad (3)$$

For systems with non-zero μ, we use Eq. (2) as the equation that determines $\mu(\rho)$ and eliminate the μ dependence in Eqs. (1) and (3), so that we can find the equation of state $P(T,\rho)$ and the energy $E(T,\rho)$

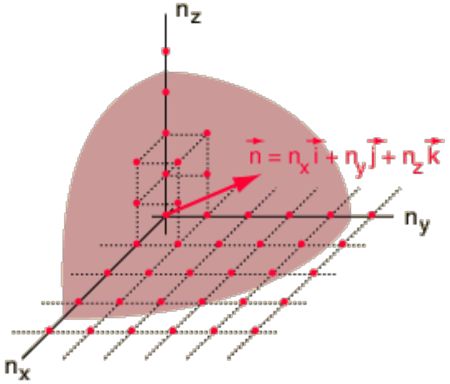
Photon gas: uncountable photons $\mu \equiv 0$

Grand-canonical partition function:

$$\Xi = \prod_{\vec{n}} \frac{1}{1 - e^{-\beta\hbar c k}}$$

Landau potential:

$$\Omega(\mathrm{T},\mathrm{V}) = -PV = \ kT \sum_{\vec{n}} \ln\left(1 - e^{-\beta\hbar c k}\right) = kT \int dn\, D(n) \ln\left(1 - e^{-\frac{\beta\hbar c}{L} n}\right)$$



Density of states

$D(n)dn = 2{\times}4\pi n^2 dn$ number of modes with quantum number between n and n+dn

$D(n)dn = D_k(k)dk = D_\omega(\omega)d\omega = D_\epsilon(\epsilon)\epsilon$

- $D_k(k) = \frac{V}{\pi^2}k^2, \quad D_\omega(\omega) = \frac{V}{\pi^2 c^3}\omega^2, \;\; D_\epsilon(\epsilon) = \frac{V}{\pi^2\hbar^3 c^3}\epsilon^2$

Pressure: $PV = -kT\int d\epsilon D(\epsilon)\log\left(1 - e^{-\beta\epsilon}\right)$

Average number of particles: $\langle N\rangle = \int d\epsilon\, D(\epsilon)\langle n\rangle_\epsilon = \int d\epsilon D(\epsilon)\frac{1}{e^{\beta\epsilon} - 1}$

Average energy: $\langle E\rangle = \int d\epsilon\, D(\epsilon)\langle n\rangle_\epsilon \epsilon = \int d\epsilon D(\epsilon)\frac{\epsilon}{e^{\beta\epsilon} - 1}$

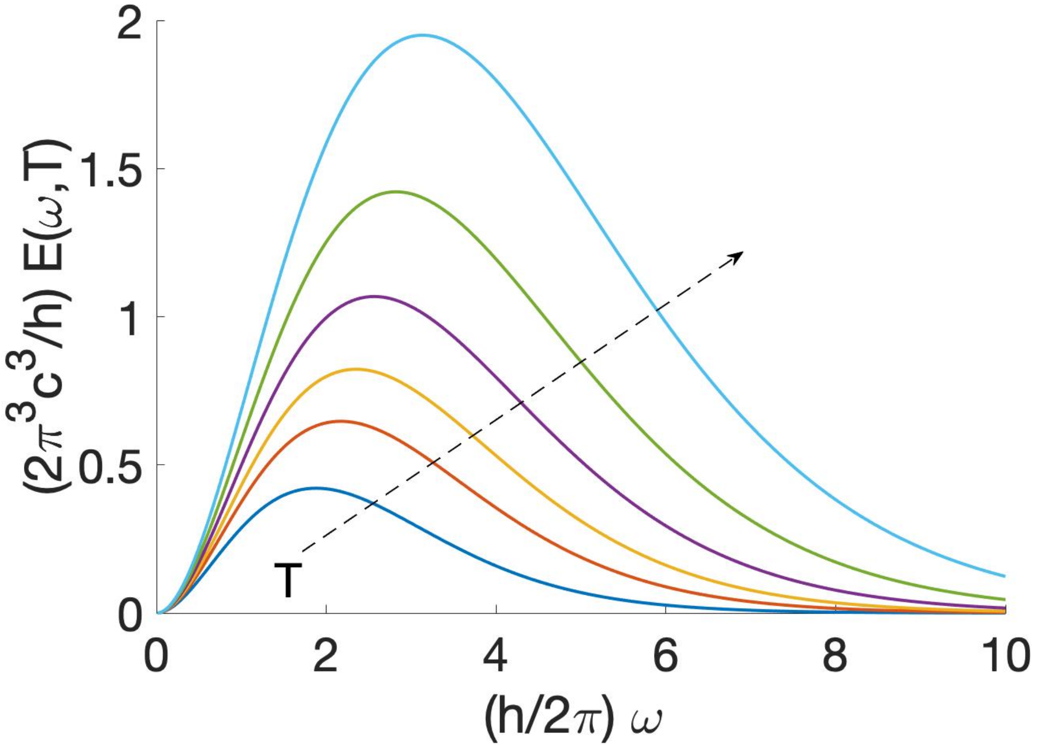
Planck distribution:

Spectral energy distribution of a photon gas

Average energy density of a photon gas:

$$\frac{\langle E\rangle(T,V)}{V} = \frac{1}{V}\int d\omega\, \frac{D_\omega(\omega)\hbar\omega}{e^{\beta\hbar\omega}-1}$$

$$= \frac{\hbar}{\pi^2 c^3}\int_0^\infty d\omega\, \frac{\omega^3}{e^{\beta\hbar\omega}-1} = \frac{\pi^2 k^4}{15 c^3 \hbar^3} T^4$$

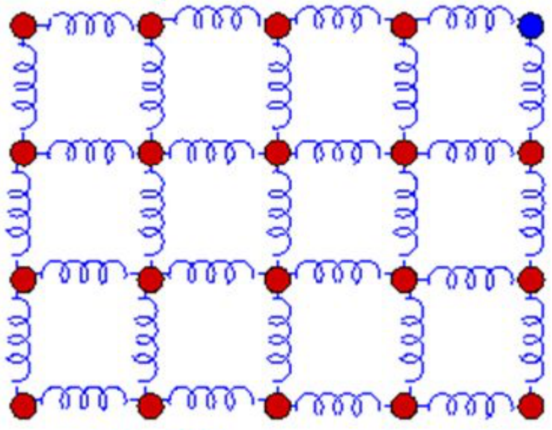


Energy per unit volume at a given frequency ω

$$\frac{\langle E\rangle}{V} = \int d\omega \mathcal{E}(\omega,T)$$

$$\mathcal{E}(\omega,T) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1}$$

Phonon gas: Debye model



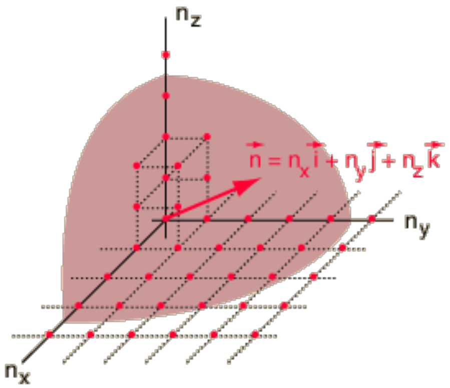
Atoms vibrate with different frequencies and a linear dispersion

$\omega = kv$, where v is the sound wave in the solid

- Density of elastic modes is analogous to the density of states for photons

(in the long-wavelength approximation, continuum elastic medium)

$$D_\omega(\omega) = 3\frac{V}{2\pi^2}\frac{\omega^2}{v^2}\frac{dk}{d\omega} = 3\frac{V}{2\pi^2}\frac{\omega^2}{v^3}, \qquad for\ \ 0 \le \omega \le \omega_D$$



- Total number of modes: $3N$ normal modes (in 3D) for N atoms

$$3N = \int_0^{\omega_D} d\omega\, D(\omega) = 3\frac{V}{2\pi^2 v^3}\int_0^{\omega_D} d\omega\, \omega^2$$

Debye frequency $\omega_D = v\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}} \to \omega_D = \frac{2\pi v}{\lambda_{\min}} = v(6\pi^2\rho)^{\frac{1}{3}}, \quad \rho = \frac{N}{V}$

Debye model: heat capacity of crystals

- Total average energy of phonons

$$U(T,V) = \int_0^{\omega_D} d\omega\, D(\omega)\, \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = 3k\, \frac{V}{2\pi^2 v^3} \int_0^{\omega_D} d\omega\, \omega^2\, \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

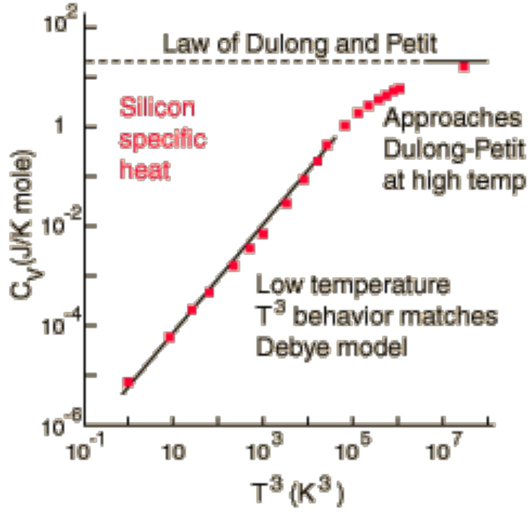
- Heat capacity

$$C_V(T) = \left(\frac{\partial U}{\partial T}\right)_V = 3k\, \frac{V}{2\pi^2 v^3} \int_0^{\omega_D} d\omega\, \omega^2 \left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

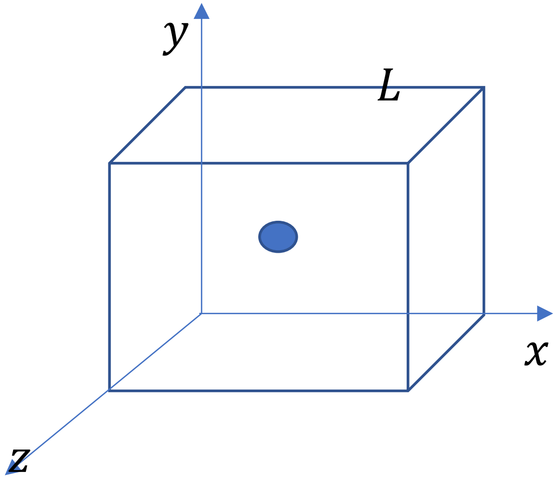
$$C_V(T) = 9Nk \left(\frac{T}{TD}\right)^3 F\left(\frac{T_D}{T}\right), \qquad F(y) = \int_0^{y} dx\, \frac{x^4 e^x}{(e^x - 1)^2}$$

$$\boldsymbol{C_V(T) \approx 3Nk, \qquad T \gg T_D}$$

$$C_V(T) \approx \frac{12}{5} Nk\pi^4 \left(\frac{T}{T_D}\right)^3, \qquad \boldsymbol{T \ll T_D}$$



Ideal Bose gas: Density of states in 3D



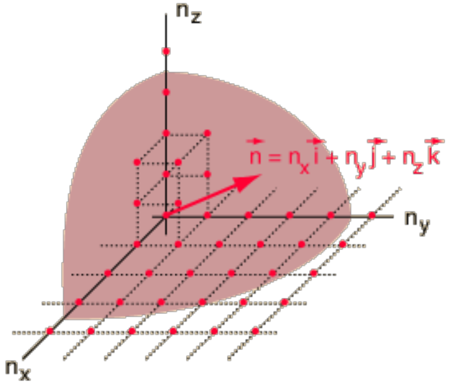
- Energy levels for a particle in a box with periodic boundary conditions:

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 |\vec{n}|^2 = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 n^2, \qquad \vec{n} = (n_x, n_y, n_z), \quad n_{x,y,z} \text{ integers}$$

- Quantum state of the particle is described by its wavefunction $\psi_1 = e^{\frac{2\pi i}{L}\vec{n}\cdot\vec{r}}$, which is determined by $\vec{n}$

Number of available states of modes between n and $n + dn$ *in 3D*

$$D(n)dn = 4\pi n^2 dn$$



$$D_\epsilon(\epsilon)d\epsilon = D(n)dn \;\rightarrow D_\epsilon(\epsilon) = \frac{V}{\sqrt{2}\pi^2}\frac{m^{3/2}}{\hbar^3}\epsilon^{\frac{1}{2}}$$

Average number of particles: $\langle N\rangle = \int d\epsilon D_\epsilon(\epsilon)\frac{1}{e^{\beta(\epsilon-\mu)}-1}$

Average energy: $U = \int d\epsilon D_\epsilon(\epsilon)\frac{\epsilon}{e^{\beta(\epsilon-\mu)}-1}$

Pressure: $PV = -kT\int d\epsilon D_\epsilon(\epsilon)\ln\left[1 - e^{-\beta(\epsilon-\mu)}\right]$

Ideal Bose gas

At a given temperature T, density ρ and chemical potential μ are related by the following equation

$$\rho(T,\mu) = \frac{1}{V}\frac{1}{\lambda^{-1}-1} + \Lambda^{-3}(T)\frac{2}{\sqrt{\pi}}\int_0^\infty dx\,\frac{x^{\frac{1}{2}}}{e^x-1}$$

$$\rho(T,\mu) = \rho_0(T,\mu) + \rho_{ex}(T,\mu), \qquad \lambda = e^{\beta\mu}$$

Critical temperature for Bose Einstein condensation:

Determined by the density of the bose gas when $\mu = \mathbf{0}$: $\quad \boldsymbol{T_c(\rho) = \frac{h^2}{2\pi m k}\left(\frac{\rho}{\zeta\left(\frac{3}{2}\right)}\right)^{\frac{2}{3}}}$

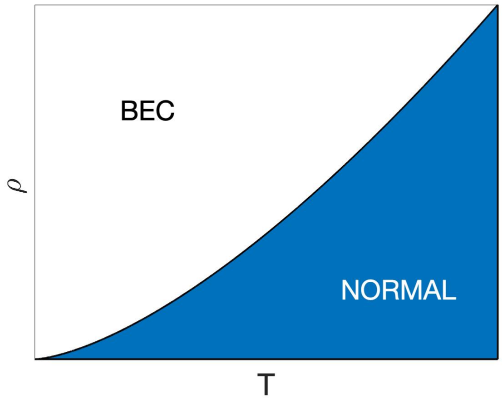
- $\boldsymbol{T \le T_c}$: ***Density is a mixture of condensed (dominant) and normal gas***

$$\boldsymbol{\rho = \rho_0(T) + \rho_{ex}(T) = \Lambda^{-3}(T_c)\zeta(3/2)}$$

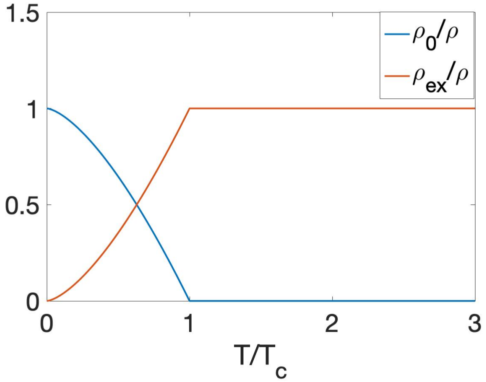
- $\boldsymbol{T > T_c}$: ***Density is dominated by that of the normal gas***

$$\boldsymbol{\rho(T,\mu) = \rho_{ex}(T,\mu) = \Lambda^{-3}(T)g_{\frac{3}{2}}(\lambda)}$$

This equation determines the chemical potential $\boldsymbol{\mu(T,\rho)}$



Bose-Einstein condensate $T < T_c$ $(\lambda = 1,\ \mu = 0)$



$$\boldsymbol{\rho = \rho_0(T) + \rho_{ex}(T) = \Lambda^{-3}(T_c)\zeta(3/2)}$$

A macroscopic fraction of particles condense into the ground state with the zero momentum

- ***Chemical potential $\mu = 0$ remains zero for all temperatures below T_c***
- ***Excess density depends only on temperature and actually decreases with decreasing temperature***
- ***Ground state density becomes non-zero and increases with decreasing temperature***

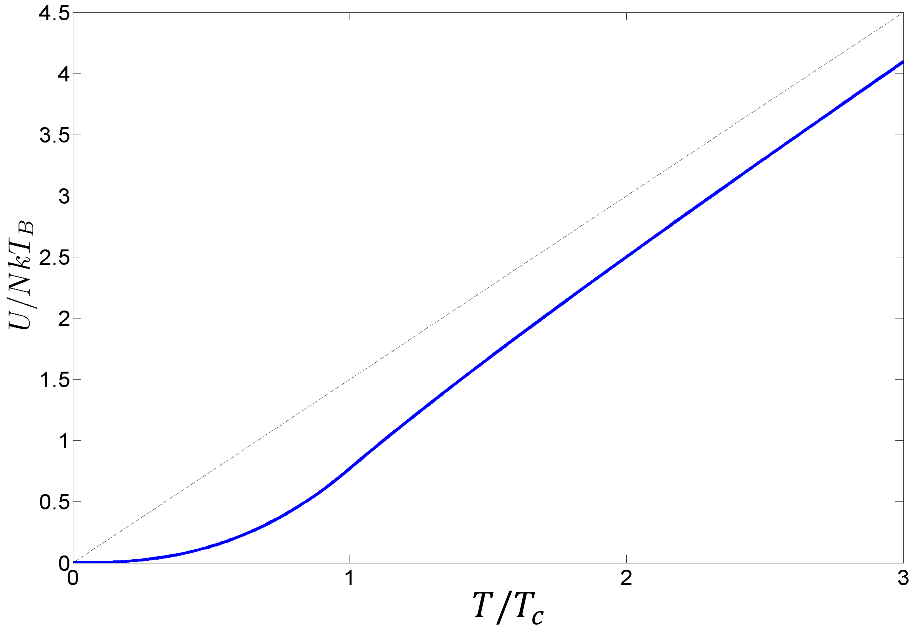
$$\frac{\rho_0}{\rho} = 1 - \frac{\rho_{ex}(T)}{\rho} = 1 - \frac{\Lambda^3(T_c)}{\Lambda^3(T)} = 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

Pressure becomes independent of density

$$\frac{P}{kT} = \frac{1}{\Lambda^3(T)} g_{5/2}(1) \rightarrow P(T) \sim T^{\frac{5}{2}}$$

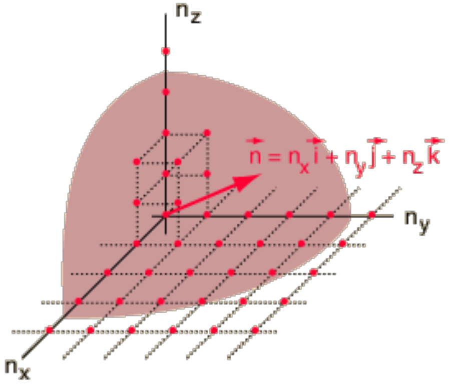
Average kinetic energy $U = \frac{3}{2} NkT\, \rho^{-1}\Lambda^{-3}(T) g_{5/2}(\lambda)$

$$U = \frac{3}{2} NkT \left(\frac{T}{T_c}\right)^{\frac{3}{2}} \frac{g_{\frac{5}{2}}(\lambda)}{\zeta\left(\frac{3}{2}\right)}, \qquad T < T_c$$



Ideal Fermi gases: Density of states in 3D

- $\Psi_1(\boldsymbol{r}) = e^{\frac{2\pi i}{L}\boldsymbol{n}\cdot\boldsymbol{r}}$ 1-particle wave function
- Each fermion (i.e. electron) has a spin moment = $\pm\frac{1}{2}$
- Energy levels a fermion in a box $V = L^3$ with periodic boundary conditions: $\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 n^2,$



Number of available states between a mode with n between n and $n + dn$: $D(n)dn = 2\times 4\pi n^2 dn$

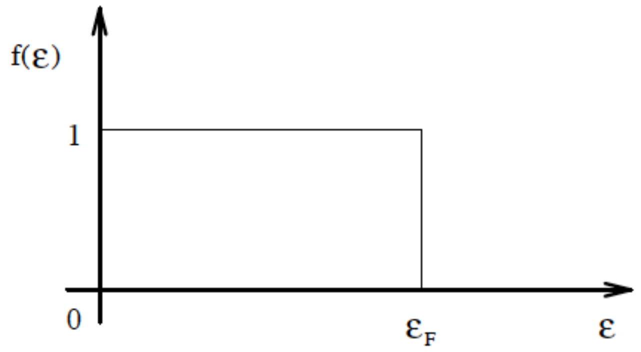
$$\sum_{\boldsymbol{n}} := 2\times\int dn\, 4\pi n^2 = \int dn\, D(n)$$

Density of states corresponding to energy ϵ:

$$D(\epsilon) = D(n)\frac{dn}{d\epsilon} \rightarrow D(\epsilon) = 2\,\frac{V}{\sqrt{2}\pi^2}\frac{m^{3/2}}{\hbar^3}\epsilon^{\frac{1}{2}}$$

The difference with respect to the density of states of bosons is the spin degeneracy of the energy levels (hence the extra factor of 2).

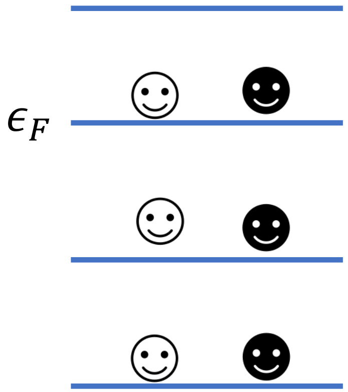
Fermi distribution at T=0 K



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

$\epsilon_F \equiv \mu$ Fermi energy level below which all states are occupied

Determined by the gas density $\epsilon_F(\rho) = \frac{\hbar^2}{2m}(3\pi^2\rho)^{\frac{2}{3}}$



$$\rho(\epsilon_F) = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon_F^{\frac{3}{2}}$$

Energy

$$\frac{\langle E\rangle_0}{V} = \frac{\sqrt{2}}{\pi^2}\frac{m^{3/2}}{\hbar^3}\int_0^{\epsilon_F} d\epsilon\, \epsilon^{\frac{3}{2}} = \frac{1}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon_F^{\frac{5}{2}}$$

Exclusion pressure

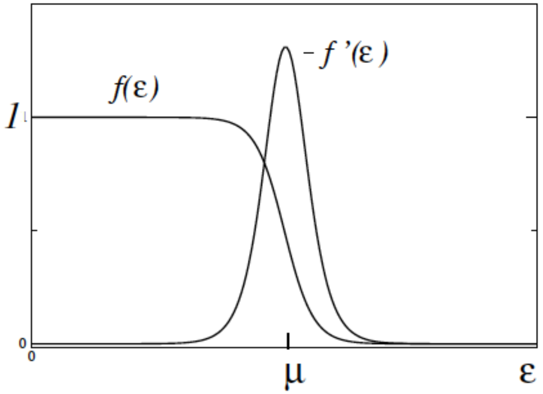
$$P_0 = \frac{\hbar^2}{15\pi^2 m^2}(3\pi^2\rho)^{\frac{5}{3}}$$

Denenerate ideal Fermi gas $T < T_F$

The Fermi temperature is most often much larges than the gas temperature

Therefore, even though the fermi gas is at finite temperature, it behaves as if it was a near zero temperature when $T \ll T_F$

Sommerfeld expansion: $\frac{kT}{\mu} \ll 1$:



$$\rho = \frac{1}{3\pi^2}\frac{(2m)^{\frac{3}{2}}}{\hbar^3}\mu^{3/2}\left(1+\frac{\pi^2}{8}\left(\frac{kT}{\mu}\right)^2+\cdots\right), \qquad \rho = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon_F^{\frac{3}{2}}$$

$$\mu = \epsilon_F\left(1-\frac{\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2+\cdots\right)$$

$$\frac{\langle E\rangle}{V} = \frac{1}{5\pi^2}\frac{(2m)^{\frac{3}{2}}}{\hbar^3}\epsilon_F^{5/2}\left(1+\frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2+\cdots\right)$$

$$\mathrm{C_V} = \frac{1}{2}\langle N\rangle\pi^2 k\frac{T}{T_F}$$

Equation of state for quantum gases: $high\, T$

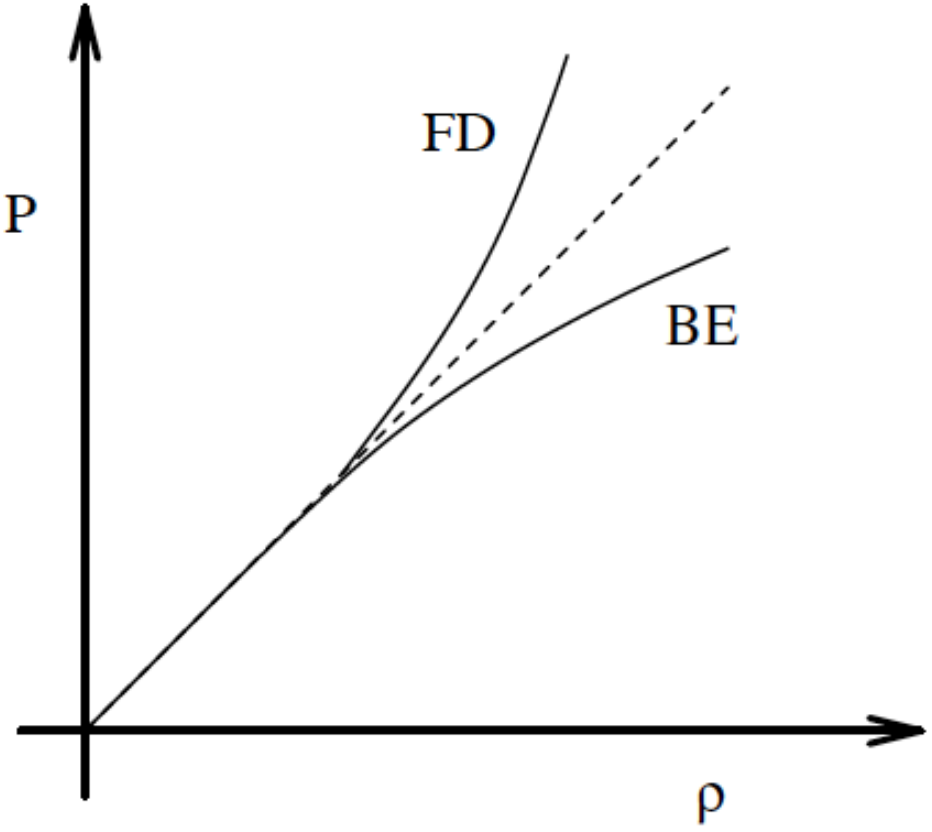
$$\mathrm{P}_{\mathrm{fermions}} \approx kT\rho\ \left(1 + 2^{-\frac{7}{2}}\Lambda^3\rho\right)$$

$$\mathrm{P}_{\mathrm{bos}ons} \approx kT\rho\ \left(1 - 2^{-\frac{5}{2}}\Lambda^3\rho\right)$$

Nonzero second virial coeff. $B_2(T) \neq 0$

Bosons: $B_2(T) < 0$ *statistical attraction*

Fermions: $B_2(T) > 0$ *statistical repulsion*

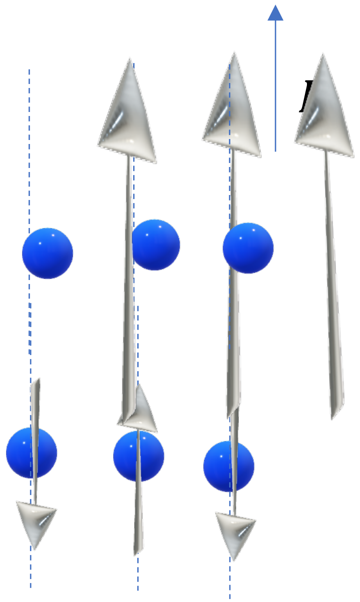


Module V: Magnetism

- Paramagnetism
- Ferromagnetism and Ising model
- Weiss mean field theory
- Ising phase transition

Ising model for ferromagnets

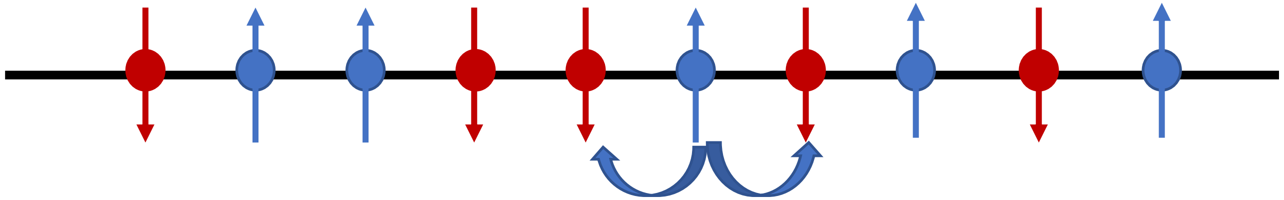
A system of N spins $s_i = \pm 1$ on a periodic lattice and in a uniform magnetic field B. Spins interact with their nearest neighbor on the lattice



$$H_N = -J \sum_{i} \sum_{\substack{j= \\ n.n.\, of\, i}} s_i s_j - \sum_{i} s_i B \,, \qquad (\mu_B = 1)$$

- $J > 0$ is the coupling constant, such that the energy is minimized when neighboring spins point in the same direction
- Summation over the nearest neighbors (n.n.) j atoms that are coupled to the ith atom on a crystal lattice (short hand notation used sometime $\equiv \langle ij \rangle$)
- The form of the spin-spin interaction as $-J s_i s_j$ originates the Coulomb interactions between the electrons (spin carriers); magnetic dipole interactions are too weak.

Ising model in 1D



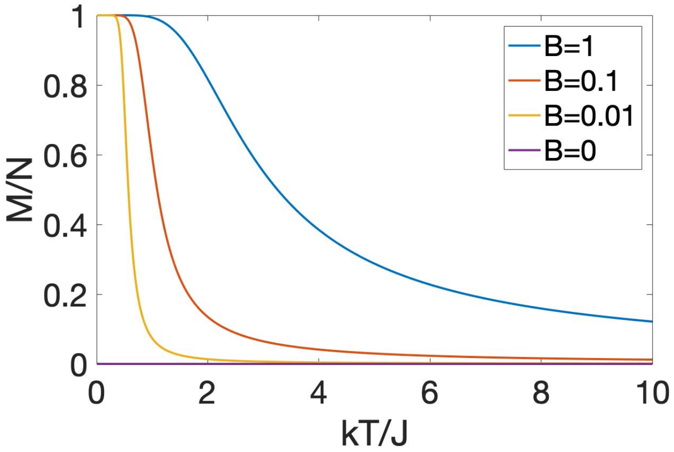
$$H_N = -J\sum_{i=0}^{N-1} s_i s_{i+1} - \sum_i s_i B\,, s_i = \pm 1$$

Periodic boundary conditions $s_N \equiv s_0$

Partition function for N spins: Transfer matrix

$$Z_N = \sum_{\{s_i\}} e^{-\beta H_N(\{s_i\})} = Tr(T^N) = \lambda_1^N + \lambda_2^N \approx \lambda_1^N, \qquad for\ N \gg 1$$

$$T = \begin{pmatrix} e^{\beta(J+B)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-B)} \end{pmatrix}$$

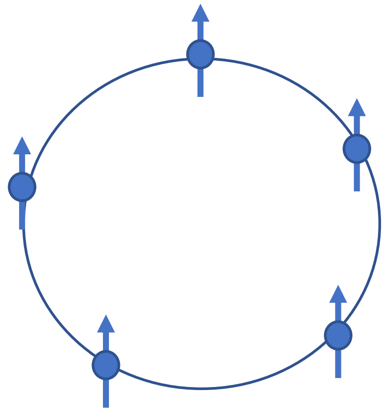


Gibbs free energy $G_N = -kT\ln(Z_N)$

Mean magnetization $M(T,B) = -\left(\frac{\partial G_N(T,B)}{\partial B}\right)_T$

Any themal fluctuation destroys the net magnetization in the limit of zero applied field

1D Ising model: No phase transition



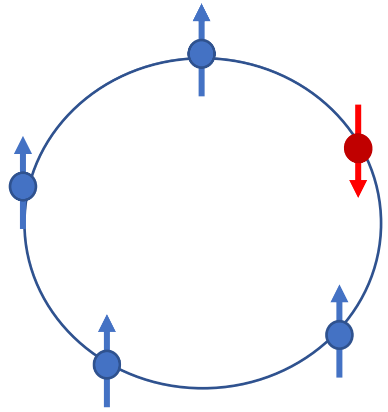
At any nonzero temperature, it is energetically favorable to create defects (kinks) due to thermal fluctuations

Change in energy for flipping a spin (kink in the ordered state)

$$U_0 = -NJ\ (order), \qquad U_1 = -(N-2)J + 2J\ (with\ a\ kink) \rightarrow \Delta U = 4J$$

Change in entropy for flipping a spin anywhere in the 1D chain (N sites)

$$\Delta S = k \log N$$

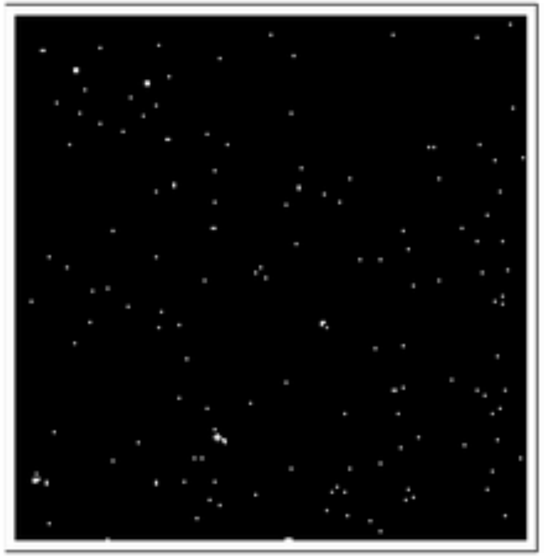


The spin flipping due to thermal fluctuations is favored when it lowers the **Helmholtz free energy**

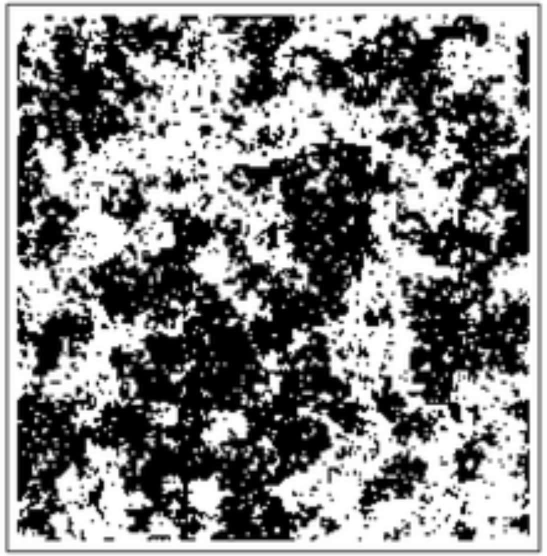
$$\Delta F = \Delta U - T\Delta S < 0 \rightarrow J - kT \log N < 0$$

This is always satisfied at any $\mathrm{T} > 0$, hence the spin order is spontaneously broken by kinks due thermal fluctuations.

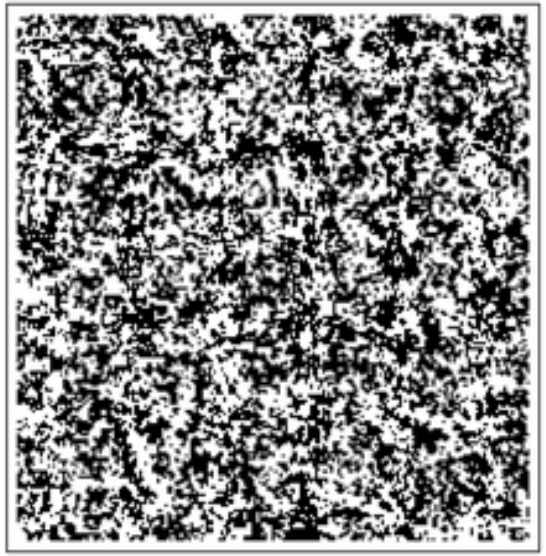
Ising model in d>1: Critical phase transitions



$T < T_C$



$T \approx T_C$



$T > T_C$

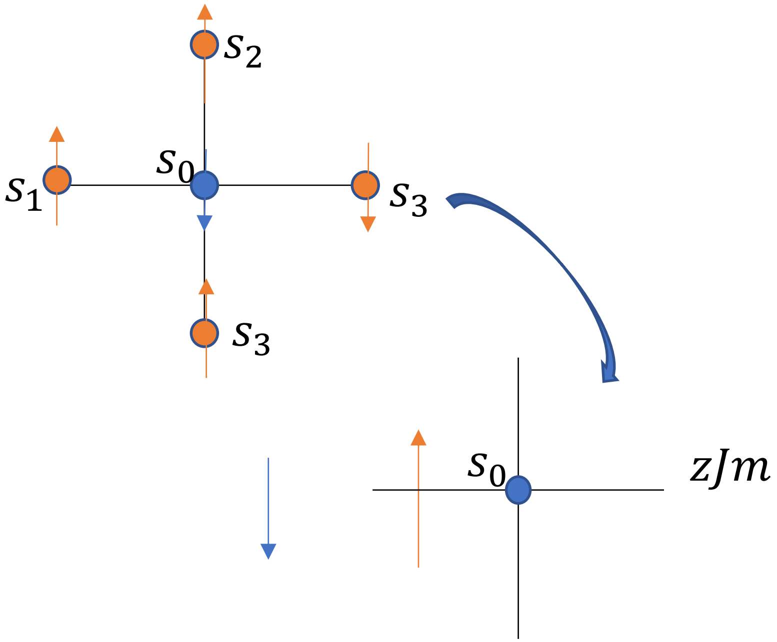
Critical phase transition occurs at a unique point in the $B - T$ diagram: (B_c, T_c)

Q: How do we *theoretically* predict this critical point and the behavior near it?

A: Mean-field approximation, Landau field theory, renormalization group techniques

Weiss mean-field theory

$$H_N = -J\sum_{\langle ij\rangle} s_i s_j - \sum_i s_i B = -\sum_i s_i\left(J\sum_{j=n.n.(i)}^{z=2d} s_j + B\right)$$



- Replace the neighboring spin s_j by the mean + fluctuations

$$s_j = m + (s_j - m) = m + \delta s_j$$

- ***Mean-field approxitimation: Ignore the effect of fluctations***

$H = -\sum_i s_i B_{eff}$, where $B_{eff} = B + zJm$

z is the coordination number; $z = 2d$ for a square lattice ($z = 4$ in 2D, $z = 6$ in 3D)

Self-consistent equation $\boldsymbol{m \equiv \langle s\rangle}$

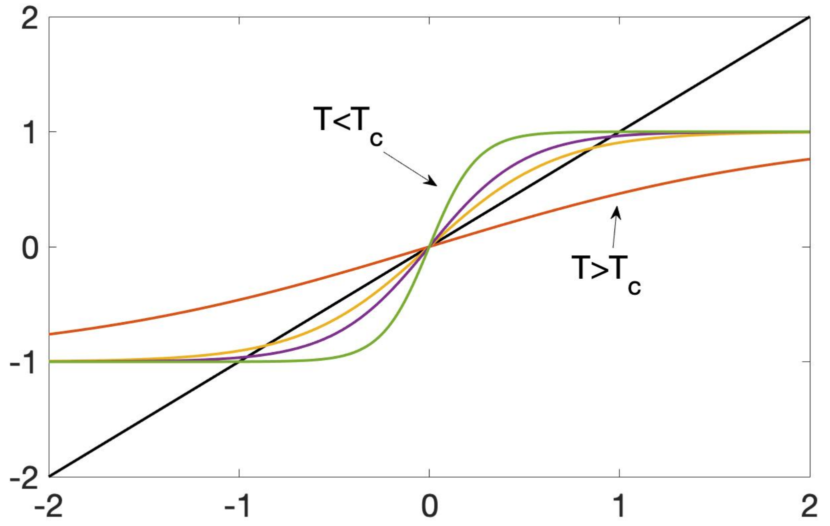
$$\boldsymbol{m = \ tanh\left[\frac{T_c}{T}m + \beta B\right]}$$

Self-consistent equation

- Limit of $B = 0$

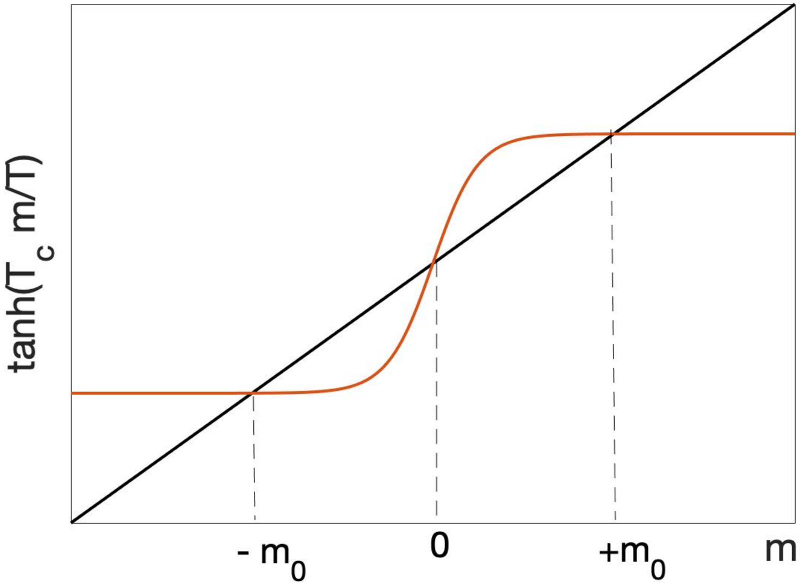
$$\boldsymbol{m} = \boldsymbol{tanh}\left[\frac{\boldsymbol{zJm}}{\boldsymbol{kT}}\right]$$

  - solved graphically by looking at the intersection points between the diagonal curve and the $\tanh(x)$



Critical temperature: $\boldsymbol{T_c} = \frac{\boldsymbol{zJ}}{\boldsymbol{k}}$

$$\boldsymbol{m} = \boldsymbol{tanh}\left[\frac{\boldsymbol{T_c}}{\boldsymbol{T}}\boldsymbol{m}\right]$$



- For $T > T_c$, there is only one root at $m = 0$
- For $T < T_c$, there are three roots at $m = 0, \pm m_0(T)$
- The non-zero solutions depend on the temperature below T_c

Critical exponents for the magnetic phase transition

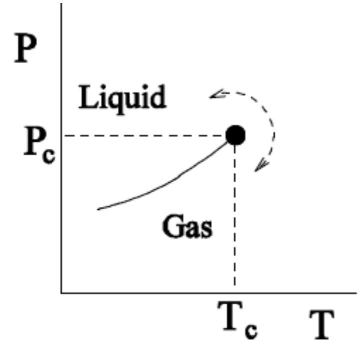
Mean-field universality class

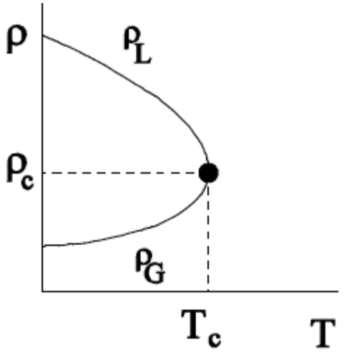
Order parameter	$M(T, B=0) \sim (T_c - T)^{\beta}, \quad \beta_{MF} = \frac{1}{2}$
Critical isotherm	$\mathrm{M}(T_c, B) \sim \lvert B\rvert^{\delta}, \quad \delta_{MF} = 3$
Susceptibility	$\chi(T, B=0) \sim \lvert T_c - T\rvert^{-\gamma}, \quad \gamma_{MF} = 1$
Heat capacity	$C_B(T, B=0) \sim \lvert T_c - T\rvert^{-\alpha}, \quad \alpha_{MF} = 0$

Exponent	2D	3D	Mean field
α	0	0.11	0
β	1/8	0.32	1/2
γ	7/4	1.24	1
δ	15	4.90	3

Mean field Ising universality class

Correspondence between magnetics and fluids





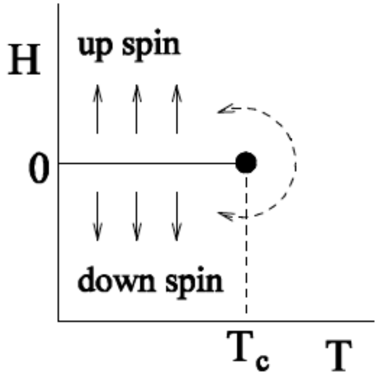
Gas-Liquid	Magnets
Volume, V or density, ρ	Mean magnetization, $-M$
Pressure, P	Magnetic field, B
Gibbs free energy, $G(P,T)$	Gibbs free energy, $G(B,T)$
Compressibility, $\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}$	Susceptibility, $\chi = \frac{\partial M}{\partial B}$
Heat capacity, $C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$	Heat capacity, $C_B = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_B$

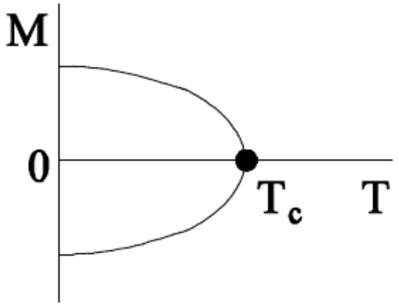
Density (Order parameter) $\rho(T,P_c) \sim (T_c - T)^{\beta}, \quad \beta_{MF} = \frac{1}{2}$

Critical isotherm $V(P,T_c) \sim P^{\delta}, \quad \delta_{MF} = 3$

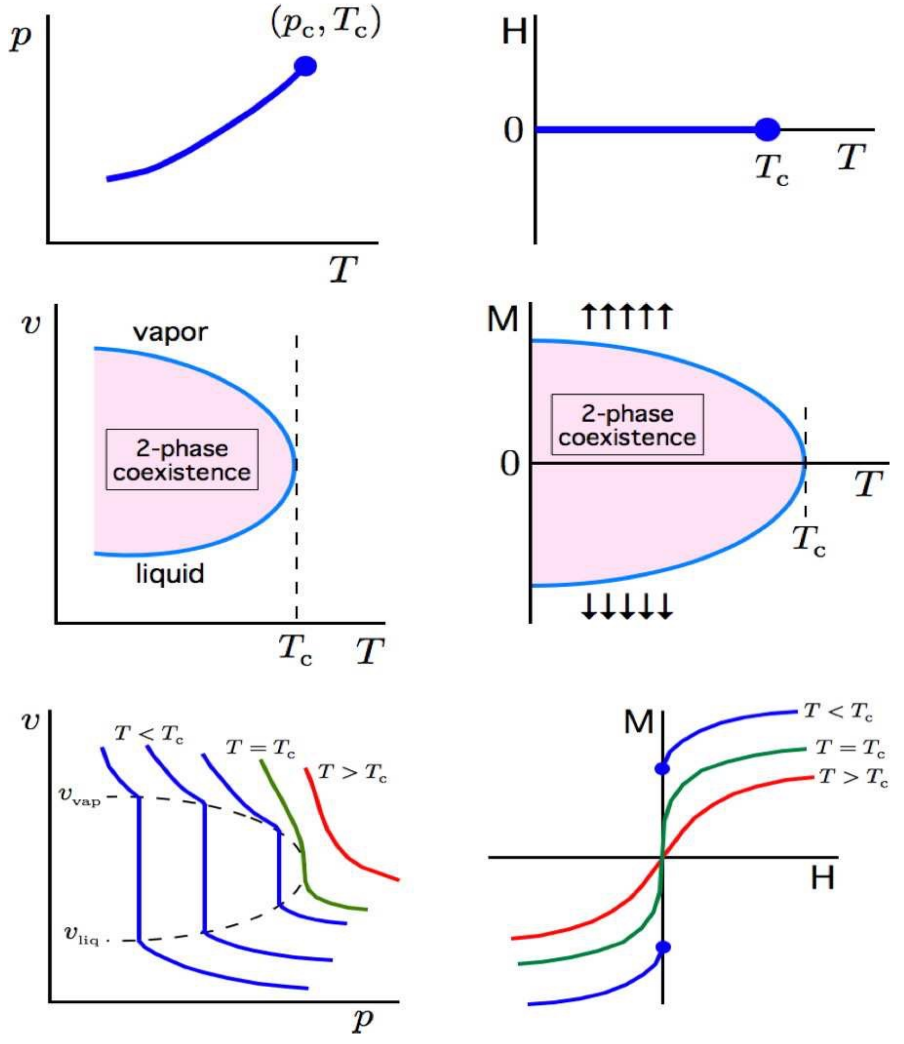
Compressibility $\kappa_T(T) \sim |T_c - T|^{-\gamma}, \quad \gamma_{MF} = 1$

Heat capacity $C_P(T) \sim |T_c - T|^{-\alpha}, \quad \alpha_{MF} = 0$





Correspondence between magnetics and fluids



Module VI: Stochastic processes and nonequilibrium statistical mechanics

- Central limit theorem
- Random walk, diffusion
- Poisson process
- Brownian motion

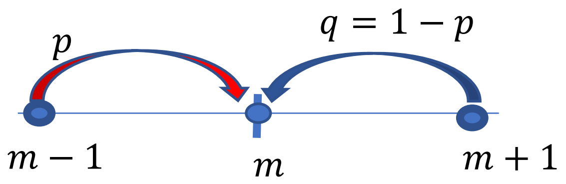
Central limit theorem: Limit distribution of sums

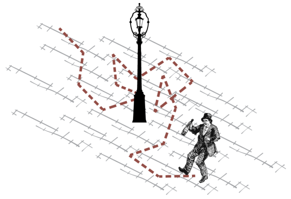
Suppose we have a set of N *independent, identically distributed (i.i.d.) variables* x_i drawn from the same parent distribution $p(x_i)$ *with*

1. *Zero mean* $\int dx\, x\, p(x) = \langle x \rangle = 0$
2. *Finite variance* $\int dx\, x^2\, p(x) = \sigma^2 < \infty$

The sum of N variables $X = \sum_{i=1}^{N} x_i$ is also a stochastic quantity which, in the limit of $N \gg 1$, is distributed according to the Gaussian distribution ***independent of the parent distributions*** $\boldsymbol{p(x_i)}$

Random walker





- For each state there are two options:
  - RW takes a left jump $m + 1 \to m$
  - RW takes a right jump $m - 1 \to m$

Particle stochastic dynamics

$$\mathrm{m_{n+1}} = \mathrm{m_n} + \Delta x_n, \quad \Delta \mathrm{x_n} = \begin{cases} +1, \text{with probability p} \\ -1, \text{with probability } q \end{cases}$$

Probability distribution function for Rsteps to the right after N steps $P_N(R) = \frac{N!}{R!(N-R)!} p^R q^{(N-R)}, \quad m = 2R - N$

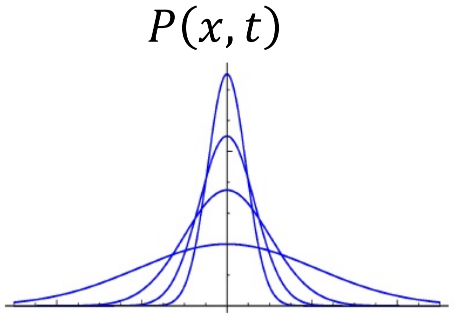
Master equation for the evolution of $P_N(m)$

$$\boldsymbol{P\,(m, N+1) = pP(m-1, N) + qP(m+1, N)}$$

Diffusion equation: continuum time and space limit of the master equation

$$\frac{\partial P(x,t)}{\partial t} = -v \frac{\partial P(x,t)}{\partial x} + D \frac{\partial^2 P(x,t)}{\partial x^2}, \qquad v = \frac{(p-q)\Delta \mathrm{x}}{\Delta t}, \qquad D = \frac{\Delta x^2}{2\Delta t}$$

$$P(x,t) = \frac{1}{\sqrt{4\pi D t}} e^{-\frac{(x-vt)^2}{4Dt}}$$



Poisson stochastic process

Describes discrete and independent random events that occur at a fixed rate, λ

Two important examples of such Poisson processes: **radioactive decay** and **death process in population dynamics**

Decay probability for one nucleus: $\boldsymbol{q_t = 1 - e^{-\lambda t}}$; **Survival probability** at time t $\mathrm{p_t} = \boldsymbol{e^{-\lambda t}}$

This is equivalent to the probability that $n = N$ nuclei **survived** the decay

$$P_t(n) = \frac{N!}{n!\,(N-n)!} p_t^n (1-p_t)^{N-n}$$

Poisson distribution: $\boldsymbol{N \to \infty, and\ p_t \to 0}$ with fixed $Np_t = \mu_t$

$$P_{\mu_t}(n) = \frac{{\mu_t}^n}{n!} e^{-\mu_t}$$

Master equation for Poisson process

i) The probability for $(n+1)$ survivers at t is $P(n+1,t)$ and probability that one of them will decay is $(n+1)q_{\Delta t}p_{\Delta t}^{n}$, hence this scenario gives a contribution $(n+1)q_{\Delta t}p_{\Delta t}^{n}P(n+1,t)$.

ii) The probability that one out of (n) will decay is the binomial distribution $nq_{\Delta t}p_{\Delta t}^{n-1}$. The probability for (n) survivers at t is $P(n,t)$ and the probability that one of them will decay is $nq_{\Delta t}p_{\Delta t}^{n-1}$, hence change in probability is proportional to $-\mathrm{n}\mathrm{q}_{\Delta t}p_{\Delta t}^{n-1}P(n,t)$.

$$P(n,t+\Delta t)=P(n,t)+(n+1)q_{\Delta t}p_{\Delta t}^{n}P(n+1,t)-\mathrm{n}\mathrm{q}_{\Delta t}p_{\Delta t}^{n-1}P(n,t)$$

Taylor expanding around t and taking the limit of $\Delta t \ll 1$

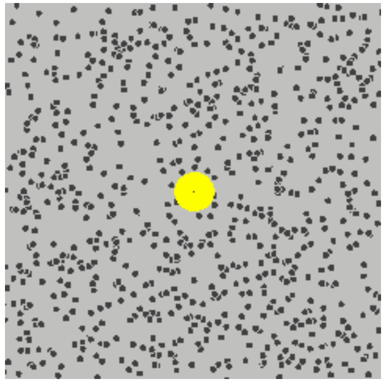
$$\frac{\partial P(n,t)}{\partial t}=\lambda(n+1)P(n+1,t)-\lambda nP(n,t), \qquad n=1,\cdots N \qquad (1)$$

Where $\frac{q_{\Delta t}}{\Delta t}=\frac{1-e^{-\lambda\Delta t}}{\Delta t}\rightarrow\lambda$ is a fixed decaying rate.

Solution of this master equation is obtain by the generating function $G(s,t)=\sum_{n=0}^{N}s^{n}\,P(n,t),\ \mathrm{s}<1$

Probability of have n surving nuclei at time t is $P(n,t)=\frac{N!}{n!(N-n)!}p_t^n(1-p_t)^{N-n},\ p_t=e^{-\lambda t}$

Brownian motion and Langevin equation



- Random motion of particles suspended in a fluid. These are also called **colloidal particles** and are much bigger in size than the fluid particles

The Brownian particle evolves by the Langevin equation. It is a generalization of the Newton’s law of motion when the Brownian particle experiences a random force through the random collisions with the fluid particles. In addition, there is a drag force because the fluid is viscous.

Langevin equation:

$$m\frac{dv}{dt} = -\alpha v + R(t)$$

$$\langle R(t)\rangle = 0$$

$$\langle R(t)R(t')\rangle = 2\alpha kT\delta(\mathrm{t}-\mathrm{t}')$$

The amplitude of the random force is determined by the local equilibrium assumption: the mean kinetic energy of the BM is the same the energy of the fluid particles (equal to the equipartition of energy)

Diffusion of the BM and Einstein's relation

$t \ll \frac{m}{\alpha}$ Ballistic Regime: on short timescales, the Brownian particles is advected by the fluid with a mean velocity determined by the kinetic energy of the fluid particles

$$\langle x(t)^2 \rangle = v_{\text{thermal}}^2 \; t^2$$

$v_{thermal} = \frac{\sqrt{\langle x(t)^2 \rangle}}{t} = \frac{kT}{m}$ from the equipartition of energy

$t \gg \frac{m}{\alpha}$ Diffusive Regime: on long timescales, the Brownian particles diffuses like a random walker

$$\langle x(t)^2 \rangle = \; 2\boldsymbol{D}t$$

Einstein's relation $\boldsymbol{D} = \frac{\boldsymbol{kT}}{\boldsymbol{\alpha}}$