Theoretical Statistical Physics (MKTP1) Version: 9.2.2021

1 Introduction to probability theory Bayes' theorem

$$p(B|A) = \frac{p(A|B) \cdot p(B)}{p(A)} = \frac{p(A|B) \cdot p(B)}{\sum_{B'} p(A|B) \cdot p(B')}$$

Expactation and covariance

$$\langle f \rangle = \sum_{i} f(i)p_{i} \text{ or } \langle f \rangle = \int f(x)p(x)dx$$

$$\mu = \langle i \rangle = \sum_{i} ip_{i} \text{ or } \mu = \langle x \rangle = \int xp(x)dx$$

$$\sigma^{2} = \langle i^{2} \rangle - \langle i \rangle^{2}$$

$$\sigma_{ij}^{2} = \langle ij \rangle - \langle i \rangle^{2}$$

Binomial distribution

$$\frac{N!}{(N-i)!i!} = \binom{n}{i} \text{ binomial coefficient}$$

$$p_i = \binom{N}{i} \cdot p^i q^{N-i} \text{ distribution}$$

$$\mu = \langle i \rangle = N \cdot p$$

$$\langle i^2 \rangle = p \cdot N + p^2 \cdot N \cdot (N-1)$$

$$\sigma^2 = N \cdot p \cdot q$$

Gauss distribution

$$p(x) = \frac{1}{\left(2\pi\sigma^2\right)^{\frac{1}{2}}} \cdot e^{-\frac{x-\mu}{2\sigma^2}}$$

$$e = \sigma^2$$

Poisson distribution

$$p(k;\mu) = \frac{\mu^k}{k!} e^{-\mu}, \quad E[k] = \mu, \ V[k] = \mu$$

Information entropy

$$S = -\sum_{i} p_{i} \ln(p_{i})$$

2 The microcanonical ensemble The fundamental postulate

$$\Omega(E) = \sum_{n:E-\delta E \le E_n \le E} 1$$

$$\Omega(E; \delta E) = \frac{1}{h^{3N} N!} \int_{n:E-\delta E \le \mathcal{H}(\vec{q}, \vec{p}) \le E} d\vec{q} d\vec{p}$$

$$S = -k_B \sum_{i=1}^{\Omega} p_i \ln(p_i) = k_B \ln(\Omega)$$

microcanonical partition sum for an ideal gas

$$\begin{split} \Omega(E) &= \frac{V^N \pi^{3N/2} (2mE)^{3N/2}}{h^{3N} N! \left(\frac{3N}{2}\right)!} \\ S &= k_B N \left\{ \ln \left[\left(\frac{V}{N}\right) \left(\frac{4\pi mE}{3h^2 N}\right)^{3/2} \right] + \frac{5}{2} \right\} \end{split}$$

Equilibrium conditions

Thermal contact

$$\left.\frac{\partial S(E,V,N)}{\partial E}\right|_{V,N} = \frac{1}{T(E,V,N)}$$

Contact with volume excahnge

$$\left. \frac{\partial S(E,V,N)}{\partial V} \right|_{E,N} = \frac{p(E,V,N)}{T(E,V,N)}$$

Contact with exchange of particle number

$$\left. \frac{\partial S(E,V,N)}{\partial N} \right|_{E,V} = -\frac{\mu(E,V,N)}{T(E,V,N)}$$

Equations of state

$$dE = TdS - pdV + \mu dN$$

Equations of state fo ideal gas

$$S = k_B N \left[\ln \left(\frac{V}{N \lambda^3} \right) + \frac{5}{2} \right] \text{ fundamental}$$

$$E = \frac{3}{2} N k_B T \qquad \text{caloric}$$

$$pV = N k_B T \qquad \text{thermal}$$

$$\mu = k_B T \ln \left(\frac{N \lambda^3}{V} \right) \text{ chemical potentail}$$

Einstein model for specific heat of a solid

$$E = \hbar\omega \left(\frac{N}{2} + Q\right)$$

$$\Omega(E, N) = \frac{(Q + N)!}{Q!N!}$$

$$S = k_B \ln(\Omega)$$

$$= k_B \left[Q \ln\left(\frac{Q + N}{Q}\right) + N \ln\left(\frac{Q + N}{N}\right)\right]$$

$$= k_B N \left[(e + \frac{1}{2}) \ln(e + \frac{1}{2}) - (e - \frac{1}{2}) \ln(e - \frac{1}{2})\right]$$

$$e = E/E_0; E_0 = N\hbar\omega$$

$$\rightarrow E = N\hbar\omega \left(\frac{1}{2} + \frac{1}{\beta}\right)$$

Entropic elasticity of polymers

$$\begin{aligned} N_{+} - N_{-} &= \frac{L}{a} \\ N_{+} &= \frac{1}{2} \left(N + \frac{L}{a} \right) \\ \Omega &= \frac{N!}{N_{+}! N_{-}!} \\ S &= -k_{B} \left(N_{+} \ln \left(\frac{N_{+}}{N} \right) + N_{-} \ln \left(\frac{N_{-}}{N} \right) \right) \end{aligned}$$

Statistical deviation from average

Two ideal gases in thermal conact $T_1 = T_2$

$$S_{i} = \frac{3}{2}k_{B}N_{i}\ln(E_{i}) + \text{independent of } E_{i}$$

$$S = S_{1} + S_{2}$$

$$dS = 0 \rightarrow \frac{\partial S_{1}}{\partial E_{1}} = \frac{\partial S_{2}}{\partial E_{2}}$$

$$\rightarrow \overline{E}_{1} = \frac{N_{1}}{N}E$$

consider small deviation:

$$E_1 = \overline{E}_1 + \Delta E, \quad E_2 = \overline{E}_2 - \Delta E$$

$$S(\overline{E}_1 + \Delta E) \approx \frac{3}{2} k_B \left[N_1 \ln \overline{E}_1 + N_2 \ln \overline{E}_2 - \frac{N_1}{2} \left(\frac{\Delta E}{\overline{E}_1} \right)^2 - \frac{N_2}{2} \left(\frac{\Delta E}{\overline{E}_2} \right)^2 \right]$$

$$\rightarrow \Omega = \overline{\Omega} e^{\left[-\frac{3}{4} \left(\frac{\Delta E}{E} \right)^2 N^2 \left(\frac{1}{N_1} + \frac{1}{N_2} \right) \right]}$$

3 The canonical ensemble Boltzmann distribution

Temperature T is fixed.

$$p_i = \frac{1}{Z}e^{-\beta E_i}$$
 Boltzmann distribution $Z = \sum_i e^{-\beta E_i}$ partition sum

For classical Hamiltonian systems:

$$p(\vec{q}, \vec{p}) = \frac{1}{ZN!h^{3N}} e^{-\beta \mathcal{H}(\vec{q}, \vec{p})}$$
$$Z = \frac{1}{N!h^{3N}} \int d\vec{q} d\vec{p} e^{-\beta \mathcal{H}(\vec{q}, \vec{p})}$$

Free energy

probability that the system has energy E

$$\begin{split} p(E) &= \frac{1}{Z} \Omega(E) e^{-\beta E} = \frac{1}{Z} e^{-\beta E + S(E)/k_B} \\ &= \frac{1}{Z} e^{-\frac{E - TS}{k_B T}} = \frac{1}{Z} e^{-\beta F} \end{split}$$

This is maximal, if F has a minimum with respect to E:

$$0 = \frac{\partial F}{\partial E} = 1 - T \frac{\partial S}{\partial E} = 1 - T \frac{1}{T_1}$$

thas is when the system is as the temperature of the heath bath. In the canonical ensemble, equilibrium cor-

responds to the minimum of the free energy
$$F(T,V,N)$$

$$\frac{1}{T}=\frac{\partial S(E,V,N)}{\partial E}$$

total differential of F(T, p, V)

$$dF = dE + d(TS)$$

$$= TdS - pdV + \mu N - TdS - SdT$$

$$= -SdT - pdV + \mu N$$

Equations of state

$$S = -\frac{\partial F}{\partial T}$$

$$p = -\frac{\partial F}{\partial V}$$

$$\mu = \frac{\partial F}{\partial N}$$
e F:

how to calculate *F*:

$$\to F(T, V, N) = -k_B T \ln(Z(T, V, N))$$

how to calculate average energy $U = \langle E \rangle$ directly from the partition sum:

$$\langle E \rangle = \sum_{i} p_{i} E_{i} = \frac{1}{Z} \sum_{i} E_{i} e^{-\beta E_{i}}$$
$$= -\partial_{\beta} \ln(Z(\beta))$$

Non-interacting systems

 ϵ_{ij} is the j^{th} state of the i^{th} element

$$Z = \sum_{j_1} \sum_{j_2} \dots \sum_{j_N} e^{-\beta \sum_{i=1}^N \epsilon_{ij_i}}$$

$$= \left(\sum_{j_1} e^{-\beta \epsilon_{1j_1}}\right) \dots \left(\sum_{j_N} e^{-\beta \epsilon_{Nj_1N}}\right)$$

$$= z_1 \cdot \dots \cdot z_N = \prod_{i=1}^N z_i$$

$$\rightarrow F = -k_B T \sum_{i=1}^{N} \ln(z_i) = -k_B T \ln(Z)$$

$$Z = z^N$$
, $F = -k_B T N ln(z)$

TODO: ADD EXAMPLES Equipartition theorem

f are the degrees of freedom. harmonic Hamiltonian with f = 2

$$\mathcal{H} = Aq^2 + Bp^2$$

$$z \propto \int dq dp e^{-\beta \mathcal{H}}$$

$$= \left(\frac{\pi}{A\beta}\right)^{\frac{1}{2}} \cdot \left(\frac{\pi}{B\beta}\right)^{\frac{1}{2}}$$

$$\propto \left(T^{\frac{1}{2}}\right)^f$$

For sufficiently high temperture (classical limit), each quadratic term in the Hamiltonian contributes a factor $T^{\frac{1}{2}}$ to the partition sum ('equipartition theorem')

$$F = -k_B T \ln(z) = -\frac{f}{2} k_B T \ln(T)$$

$$S = -\frac{\partial F}{\partial T} = \frac{f}{2} k_B (\ln(T) + 1)$$

$$U = -\partial_\beta \ln(z) = \frac{f}{2} k_B T$$

$$c_v = \frac{dU}{dT} = \frac{f}{2} k_B$$

Molecular gases

$$Z = Z_{trans} \cdot Z_{vib} \cdot Z_{rot} \cdot Z_{elec} \cdot Z_{nuc}$$
$$Z_x = z_x^N$$

Vibrational modes

often described by the Morse potential:

$$V(r) = E_0 \left(1 - e^{-\alpha(r - r_0)} \right)^2$$

An exact solution of the Schrödinger equation gives:

$$E_n = \hbar\omega_0 \left(n + \frac{1}{2}\right) - \frac{\hbar^2 \omega_0^2}{eE_0} \left(n + \frac{1}{2}\right)^2$$
$$\omega_0 = \frac{\alpha}{2\pi} \sqrt{\frac{2E_0}{\mu}}, \quad \mu = \frac{m}{2}$$

For $\hbar\omega_0\ll E_0$ we can use the harmonic approximation:

$$z_{vib} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega_0}}$$

$$T_{vib} \approx \frac{\hbar\omega_0}{k_B} \approx 6.140 \text{K for } H_2$$

Rotational modes

standart approximation is the one of a rigid rotator. The moment of inertia is given as:

$$I = \mu r_0^2 \quad T_{rot} = \frac{\hbar^2}{I k_B}$$

$$\rightarrow E_l = \frac{\hbar^2}{2I} l(l+1)$$

Nuclear contributions: ortho- and parahydrogen

$$z_{ortho} = \sum_{l=1,3,5,...} (2l+1)e^{-\frac{l(l+1)T_{rot}}{T}}$$
$$z_{para} = \sum_{l=0,2,4} (2l+1)e^{-\frac{l(l+1)T_{rot}}{T}}$$

Theoretical Statistical Physics (MKTP1)

Specific heat of a solid

Version: 9.2.2021

Debye model

$$\rightarrow \omega(k) = \left(\frac{4\kappa}{m}\right)^{\frac{1}{2}} \left| \sin\left(\frac{ka}{2}\right) \right|$$
$$\omega = \frac{2\pi}{T}, \quad k = \frac{2\pi}{\lambda}$$

Debye frequency:

$$\omega_D = c_s \left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$$

$$c_s = \left.\frac{d\omega}{dk}\right|_{k=0} = \sqrt{\frac{\kappa}{m}}a$$

density of states in ω -space:

$$D(\omega) = 3\frac{\omega^2}{\omega_D^3} \quad \text{for } \omega \le \omega_D$$

count modes in frequency-space:

$$\sum_{modes}(\dots) = 3\sum_k(\dots) = 3N\int_0^{\omega_D}d\omega D(\omega)(\dots)$$

partition sum:

$$z(\omega) = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

$$c_{v}(T) = \frac{\partial E}{\partial T}$$

$$= \frac{3\hbar^{2}N}{k_{B}T^{2}} \int_{0}^{\omega_{D}} d\omega \frac{3\omega^{2}}{\omega_{D}^{3}} \frac{e^{\beta\hbar\omega}\omega^{2}}{\left(e^{\beta\hbar\omega} - 1\right)^{2}}$$

$$c_v(T) = \frac{9Nk_B}{u_m^3} \int_0^{u_m} \frac{e^u u^4}{(e^u - 1)^2} du$$

the limit for $\hbar\omega_D \ll k_B T$:

$$c_v(T) = 3Nk_B$$

the limit for $k_BT \ll \hbar\omega_D$: $(T_D = \frac{\hbar\omega_D}{k_B})$

$$c_v(T) = \frac{12\pi^4}{5} N k_B \left(\frac{T}{T_D}\right)^3$$

Black body radiation

$$E = \frac{4\sigma}{c}VT^4, \quad \sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2}$$
$$c_v = \frac{16\sigma}{c}VT^3$$

$$J = \frac{P}{A} = \sigma T^4$$
 Stefan- Boltzmann law

Plank's law for black body radiation

$$u(\omega) := \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar \omega/(k_B T)} - 1}$$

The Plank distribution has a maximum at:

$$\hbar\omega_{max} = 2.82k_BT$$
 Wien's displacement law

4 The grandcanonical ensemble **Probability distribution**

T and μ are fixed.

$$p_i = \frac{1}{Z_G} e^{-\beta(E_i - \mu N_i)} \text{ prob. distribution}$$

$$Z_G = \sum_i e^{-\beta(E_i - \mu N_i)} \text{ partition sum}$$

 $\Psi = -k_B T \ln(Z_G)$ thermodynamic potential

Grandcanonical potential

The probability to have a macroscopic value (E,N) is:

$$p(E,N) = \frac{1}{Z_G} \Omega(E,N) e^{-\beta(E-\mu N)}$$
 two particles that are d states with energies 0 and
$$= \frac{1}{Z_G} e^{-\beta(E-TS-\mu N)} = \frac{1}{Z_G} e^{-\beta\Psi(T,V,\mu)}$$
 $Z_F = e^{-\beta\varepsilon}$ Fermi-Dirac

grandcanonical potential:

$$\Psi(T, V, \mu) := E - TS - \mu N$$

p is maximal, if Ψ is minimal. Total differential:

$$d\Psi = d(E - TS - \mu N)$$

$$= TdS - pdV + \mu dN - d(TS + \mu N)$$

$$= -SdT - pdV - Nd\mu$$

Equations of state:

$$S=-\frac{\partial \Psi}{\partial T}, p=-\frac{\partial \Psi}{\partial V}, N=-\frac{\partial \Psi}{\partial \mu}$$

Fluctuations

$$\langle N \rangle = \sum_{i} p_{i} N_{i} = \frac{1}{\beta} \partial_{\mu} \ln(Z_{G})$$

$$\sigma_{N}^{2} = \langle N^{2} \rangle - \langle N \rangle^{2} = \frac{1}{\beta^{2}} \partial_{\mu}^{2} \ln(Z_{G})$$

$$\frac{\sigma_{N}}{\langle N \rangle} \propto \frac{1}{N^{\frac{1}{2}}}$$

Ideal gas

$$\begin{split} Z(T,V,N) &= \frac{1}{N!} \left(\frac{V}{\lambda^3}\right)^N, \ \lambda = \frac{h}{(2\pi m k_B T)^{\frac{1}{2}}} \\ Z_G &= \sum_{N=0}^{\infty} Z(T,V,N) e^{\beta \mu N} \\ &= \sum_{N=0}^{\infty} \frac{1}{N!} \left(e^{\beta \mu} \frac{V}{\lambda^3}\right)^N \\ &= e^{z} \frac{V}{\lambda^3} \quad \text{fugacity: } z := e^{\beta \mu} \\ \langle N \rangle &= \frac{1}{\beta} \partial_{\mu} \ln(Z_G) = \frac{V}{\lambda^3} d^{\beta \mu} \\ \mu &= k_B T \ln \left(\frac{N \lambda^3}{V}\right) \end{split}$$
 Molecular adsorption onto a surface

Molecular adsorption onto a surface

$$\begin{split} Z_G &= z_G^N; z_G = 1 + e^{-\beta(\epsilon - \mu)} \\ \langle n \rangle &= \frac{1}{e^{-\beta(\mu - \epsilon)} + 1} \; \text{ per site} \\ \langle \epsilon \rangle &= \epsilon \langle n \rangle \end{split}$$

5 Quantum fluids Fermion vs. bosons

Particles with half-integer (integer) spin are called fermions (bosons). Their total wave function (space and spin) must be antisymmetric (symmetric) under the exchange of any pair of identical particles. Canonical ensemble

two particles that are distributed over two

states with energies 0 and ϵ

$$Z_B = 1 + e^{-\beta \epsilon} + e^{-2\beta \epsilon}$$
 Bose-Einstein

$$Z_M = \frac{1 + 2e^{-\beta\epsilon} + e^{-2\beta\epsilon}}{2}$$
 Maxwell-Boltzmann

Grand canonical ensemble

Fermions:

$$z_F = 1 + e^{-\beta(\epsilon - \mu)}$$

average occupation number n_E :

$$n_F = \frac{1}{e^{\beta(\epsilon - \mu)} + 1}$$
 Fermi function

For $T \rightarrow 0$, the fermi function approaches a step function:

$$n_F = \Theta(\mu - \epsilon)$$

Bosons:

$$z_B = \frac{1}{1 - e^{-\beta(\epsilon - \mu)}}$$

average occupation number n_B :

$$n_B = \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$$

- Fermions tend to fill up energy states one after the other
- Bosons tend to condense all into the same low energy state

The ideal Fermi fluid

density of states:

$$D(\epsilon) = \frac{V}{2\pi N} \left(\frac{2m}{\hbar^2}\right)^{\frac{2}{2}} \sqrt{\epsilon}$$

Fermi energy

$$N = \sum_{\vec{k}, m_S} n_{\vec{k}, m_S} = N \int_0^\infty d\epsilon D(\epsilon) n_F(\epsilon)$$

Limit $T \rightarrow 0$. $\mu(T = 0)$ is called Fermi energy:

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

specific heat

$$\mu = \epsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 \right] \text{ for } T \ll \frac{\epsilon_F}{k_B}$$

$$c_V = \left. \frac{\partial E}{\partial T} \right|_V = N \frac{\pi^2}{3} k_B^2 D(\epsilon_F) T$$

$$c_V = N \frac{\pi^2}{2} \frac{k_B T}{\epsilon_F} k_B$$

Fermi pressure

$$p \stackrel{T \to 0}{\to} \frac{2}{5} \frac{N}{V} \epsilon_F = \frac{(2\pi^2)^{\frac{2}{3}}}{5} \frac{\hbar^2}{mv^{\frac{5}{3}}}$$

The ideal Bose fluid

 $\epsilon = \frac{\hbar^2 k^2}{2m}$ and conserved particle number N.

$$N = \frac{N}{\lambda^3} g_{\frac{3}{2}}(z)$$

$$z = e^{\beta \mu}, \ \lambda = \frac{h}{(2\pi m k_B T)^{\frac{1}{2}}}$$

$$T_c = \frac{2\pi}{\left(\zeta\left(\frac{3}{2}\right)\right)^{\frac{3}{2}}} \frac{\hbar^2 \rho^{\frac{2}{3}}}{k_B m}$$

$$E = \frac{3}{2}k_B T \frac{V}{\lambda^3} g_{\frac{5}{2}}(z) = \frac{3}{2}k_B T N_e \frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)}$$

$$c_V = \frac{15}{4} k_B N \left(\frac{T}{T_c}\right)^{\frac{3}{2}} \frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} \left(\text{ for } T \leq T_c \right)$$

$$c_V = \frac{15}{4} k_B N \frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} - \frac{9}{4} k_B N \frac{g_{\frac{3}{2}}(z)}{g_{\frac{1}{2}}(z)} \left(T > T_c\right)$$

 $\mu \to -\infty$ the two grandcanonical distr. become the Maxwell-Boltzmann distr.

$$n_{F/B} = \frac{1}{e^{\beta(\epsilon - \mu)} \pm 1} \rightarrow e^{\beta\mu} e^{-\beta\epsilon}$$

$$N = g \frac{V}{\lambda^3} e^{\beta\mu}$$

$$E = \frac{3}{2} k_B T N$$

Ising model

6 Phase transitions

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j - B\mu \sum_i S_i$$

$$\beta \mathcal{H} = -K \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i$$

$$K = \beta J, \quad H = \beta B\mu$$

$$Z_N(K, H) = \sum_{S_1 = \pm 1} \dots \sum_{S_N = \pm 1} e^{-\beta \mathcal{H}} = \sum_{\{S_i\}} e^{-\beta \mathcal{H}}$$

examples:

Ferromagnetic systems:

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \vec{J}_i \vec{J}_j - \mu \vec{B} \sum_i \vec{J}_i$$

lattice gases:

$$\mathcal{H} = -\sum_{\langle i,j\rangle} J_{ij} S_i S_j$$

magnetisation

$$M(K,H) = \left\langle \mu \sum_{i=1}^{N} S_i \right\rangle$$

The 1D Ising model

$$Z_N \stackrel{N \gg 1}{\approx} (2 \cosh(K))^N$$

$$F = -k_B T N \ln \left(2 \cosh \left(\frac{J}{k_B T} \right) \right)$$

$$\langle S_i S_{i+j} \rangle = (\tanh(K))^j = \left(e^{\ln(\tanh(K))} \right)^j = e^{-j/\zeta}$$

 $\zeta = -(\ln(\tanh(K)))^{-1}$ correlation length

Transfer matrix

$$T_{i,i+1} = e^{KS_i S_{i+1} + \frac{1}{2} H(S_i + S_{i+1})}$$

$$\rightarrow e^{-\beta \mathcal{H}} = T_{1,2} \cdot T_{2,3} \dots T_{N,1}$$

$$T = \begin{pmatrix} T(+1,+1) & T(+1,-1) \\ T(-1,+1) & T(-1,-1) \end{pmatrix}$$

$$Z_N = \lambda_1^N + \lambda_2^N$$

Renormalization of the Ising chain

$$K' = \frac{1}{2} \ln(\cosh(2K))$$

Renormalization of the 2d Ising model

$$\overline{K}' = K' + K_1 = \frac{3}{8} \ln(\cosh(4K))$$

The 2d Ising model

$$\beta \mathcal{H} = -K \sum_{r,c} S_{r,c} S_{r+1,c} - K \sum_{r,c} S_{r,c} S_{r,c+1}$$

$$1 = \sinh(2K_c)$$

$$K_c = \frac{1}{2} \ln\left(1 + \sqrt{2}\right) \approx 0.4407$$

$$T_c = 2J/\ln\left(1 + \sqrt{2}\right) \approx 2.269J/k_B$$

Perturbation theory

 $F \le F_u = F_0 + \langle \mathcal{H}_1 \rangle_0$ Bogoliubov inequality

Mean field theory for the Ising model

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j$$

$$\mathcal{H}_0 = -B \sum_i S_i$$

$$F_0 = -Nk_B T \ln \left(e^{\beta B} + e^{-\beta B} \right)$$

$$= -Nk_B T \ln(2 \cosh(\beta B))$$

$$F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$$

$$= -Nk_B T \ln(2 \cosh(\beta B)) - N \frac{z}{2} \langle S \rangle_0^2$$

$$+ N \langle S \rangle_0 = F_u$$

$$\to z = 2 \cdot \text{dimension}$$

$$B = Jz \langle S \rangle_0 = Jz \tanh(\beta B)$$

$$K_c = \frac{1}{z} \to T_c = \frac{zJ}{k_B}$$

7 Classical fluids

Virial expansion

$$F = Nk_BT \left[\ln(\rho \lambda^3) - 1 + B_2 \rho \right]$$
$$p = \rho k_BT \left[1 + B_2 \rho \right]$$

Second virial coefficient

$$B_2(T) = -2\pi \int r^2 dr \left(e^{-\beta U(r)} - 1 \right)$$

8 Others

Stirling's formula

$$\ln(n!) = n \ln(n) - n + \frac{1}{2} \ln(2\pi n)$$

de Broglie relation

$$\epsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$