

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

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

$$\mu = \langle i \rangle = \sum_i i p_i \text{ or } \mu = \langle x \rangle = \int x p(x) dx$$

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

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

Binomial distribution

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

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

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

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

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

$$\sum_{i=0}^N p_i = \sum_{i=0}^N \binom{N}{i} \cdot p^i q^{N-i} = (p+q)^N = 1$$

Gauss distribution

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

Poisson distribution

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

Information entropy

$$S = - \sum_i p_i \ln(p_i)$$

2

The microcanonical ensemble

$E \approx \text{const}$  ,  $V = \text{const}$  ,  $N = \text{const}$ .

The fundamental postulate

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

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

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

$n_0$  different particles

$$\Omega = \frac{1}{h^{3N} \prod_{j=0}^{n_0} N_j!} \iint_{E-\delta E \leq \mathcal{H}(\vec{q},\vec{p}) \leq E} d\vec{q}d\vec{p}$$

Equilibrium conditions

Entropy  $S$  must be maximal

Thermal contact

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

Contact with volume exachnge

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

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

$$dE = T dS - p dV + \mu dN$$

Specific heat

$$c_v = \frac{dE}{dT}$$

solution concept

- Set up Hamiltonian
- Calculate phasevolume  $\Omega$
- Calculate entropy  $S$
- determine  $T,p,\mu$
- Calculate  $U = \langle E \rangle$
- thermodynamic potentials:

$$F(T,V,N) = U - TS$$

$$\dot{H}(S,p,N) = U + pV$$

$$G(T,p,N) = U + pV - TS$$

Ideal Gas

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + V(q_1,\dots,q_{3N})$$

microcanonical partition sum for an ideal gas

$$\Omega(E) = \frac{V^N \pi^{3N/2} (2mE)^{3N/2}}{h^{3N} N! \left(\frac{3N}{2}\right)!}$$

$$S = k_B N \left\{ \ln \left[ \left( \frac{V}{N} \right) \left( \frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} \right\}$$

Equations of state fo ideal gas

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N,V} = \frac{3}{2} \frac{Nk_B}{E} \rightarrow U = \frac{3}{2} Nk_B T$$

$$p = T \left( \frac{\partial S}{\partial V} \right)_{E,N} = TNk_B \frac{1}{V} \rightarrow pV = Nk_B T$$

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

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} \quad \text{Thermische de Broglie}$$

Einstein model for specific heat of a solid

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

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

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

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

$$e = E/E_0 \text{ ; } E_0 = N \hbar \omega \text{ ; } \beta = \hbar \omega / k_B T$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} \Rightarrow E = N \hbar \omega \left( \frac{1}{2} + \frac{1}{e^{\beta} - 1} \right)$$

Entropic elasticity of polymers

$$N_+ - N_- = \frac{L}{a} = m \rightarrow N_+ = \frac{1}{2} (N + m)$$

$$\Omega = \frac{N!}{N_+!N_-!} = \frac{N!}{\left(\frac{1}{2}(N+m)\right)!\left(\frac{1}{2}(N-m)\right)!}$$

if both directions are possible x2

$$S = -k_B \left( N_+ \ln \left( \frac{N_+}{N} \right) + N_- \ln \left( \frac{N_-}{N} \right) \right)$$

Statistical deviation from average

Two ideal gases in thermal conact  $T_1 = T_2$

$$S_i = \frac{3}{2} k_B N_i \ln(E_i) + \text{independent of } E_i$$

$$S = S_1 + S_2$$

$$dS = 0 \rightarrow \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$

$$\rightarrow \bar{E}_1 = \frac{N_1}{N} E$$

consider small deviation:

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

$$S(\bar{E}_1 + \Delta E) \approx \frac{3}{2} k_B \left[ N_1 \ln \bar{E}_1 + N_2 \ln \bar{E}_2 \right.$$

$$\left. - \frac{N_1}{2} \left( \frac{\Delta E}{\bar{E}_1} \right)^2 - \frac{N_2}{2} \left( \frac{\Delta E}{\bar{E}_2} \right)^2 \right]$$

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

3

The canonical ensemble

$T = \text{const}$  ,  $V = \text{const}$  ,  $N = \text{const}$ .

Boltzmann distribution

$$p_i = \frac{1}{Z} e^{-\beta E_i} \quad \text{Boltzmann distribution}$$

$$Z = \sum_i e^{-\beta E_i} \quad \text{partition sum}$$

For classical Hamiltonian systems:

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

$$Z_N(T,V) = \frac{1}{N!h^{3N}} \iint d\vec{q}d\vec{p} e^{-\beta \mathcal{H}(\vec{q},\vec{p})}$$

For common Hamiltonian:

$$Z_N(T,V) = \frac{1}{\lambda^{3N} N!} \int_V d\vec{q} e^{-\beta \hat{V}(\vec{q})}$$

Free energy

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

$$\langle E \rangle = U = -\partial_{\beta} \ln Z_N$$

total differential:

$$dF = dE + d(TS) = -SdT - pdV + \mu dN$$

equations of state

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

Non-interacting systems

$\epsilon_{ij}$  is the  $j^{th}$  state of the  $i^{th}$  element

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

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

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

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

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

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 Hamilto-

nian 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

$N$  molecules;  $x$  different mode types:

$$Z = Z_{trans} \cdot Z_{vib} \cdot Z_{rot} \cdot Z_{elec} \cdot Z_{nuc}$$

$$Z_x = z_x^N$$

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:

$$E_n = \hbar \omega_0 \left( n + \frac{1}{2} \right) - \frac{\hbar^2 \omega_0^2}{e E_0} \left( n + \frac{1}{2} \right)^2$$

$$\omega_0 = \frac{\alpha}{2\pi} \sqrt{\frac{2E_0}{\mu}}, \quad \mu = \frac{m}{2}$$

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

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

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

Rotational modes

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

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

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

**Nuclear contributions: ortho- and parahydro-gen**

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

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

Specific heat of a solid

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  $\omega$ -space:

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

count modes in frequency-space:

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

partition sum:

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

$$\begin{aligned} \rightarrow Z &= \prod_{modes} z(\omega) \\ \rightarrow E &= -\partial_\beta \ln(Z) = \sum_{modes} \hbar\omega \left( \frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2} \right) \\ &= E_0 + 3N \int_0^{\omega_D} d\omega \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \frac{3\omega^2}{\omega_D^3} \\ c_v(T) &= \frac{\partial E}{\partial T} \\ &= \frac{3\hbar^2 N}{k_B T^2} \int_0^{\omega_D} d\omega \frac{3\omega^2}{\omega_D^3} \frac{e^{\beta\hbar\omega} \omega^2}{\left( e^{\beta\hbar\omega} - 1 \right)^2} \\ u &= \beta\hbar\omega \\ c_v(T) &= \frac{9Nk_B}{u_m^3} \int_0^{u_m} \frac{e^u u^4}{(e^u - 1)^2} du \end{aligned}$$

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

$$c_v(T) = 3Nk_B$$

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

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

### Black body radiation

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

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

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:  
 $\hbar\omega_{max} = 2.82k_B T$     Wien's displacement law

### 4 The grandcanonical ensemble

$T, \mu = const.$

$$\begin{aligned} p_N(q,p) &= \frac{1}{\Xi_\mu(T,V)} e^{-\beta(H_N(q,p) - \mu N)} \\ \Xi_\mu(T,V) &= \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \iint d^{3N}q d^{3N}p e^{-\beta(H_N - \mu N)} \\ \rightarrow \Xi_z &= \sum_{N=0}^{\infty} z^N Z_N(T,V) \\ z &= e^{\beta\mu} \rightarrow \text{Fugacity} \end{aligned}$$

### Mean phase space observable

$$\begin{aligned} \langle F \rangle &= \frac{1}{\Xi_\mu(T,V)} \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \iint d^{3N}q d^{3N}p \dots \\ &\dots e^{-\beta(H_N - \mu N)} F_N(q,p) \end{aligned}$$

### mean particle number:

$$\begin{aligned} \langle N \rangle &= \frac{1}{\beta} \left( \frac{\partial}{\partial \mu} \ln(\Xi_\mu(T,V)) \right)_{T,V} \\ &= z \left( \frac{\partial}{\partial z} \ln(\Xi_z(T,V)) \right)_{T,V} \end{aligned}$$

### pressure:

$$p = - \left( \frac{\partial H}{\partial V} \right) = \frac{1}{\beta} \left( \frac{\partial}{\partial V} \ln(\Xi_\mu(T,V)) \right)$$

### energy $U$ :

$$\begin{aligned} U = \langle H \rangle &= - \left( \frac{\partial}{\partial \beta} \ln(\Xi_\mu(T,V)) \right)_{\mu,V} + \mu \langle N \rangle \\ &= - \left( \frac{\partial}{\partial \beta} \ln(\Xi_z(T,V)) \right)_{z,V} \end{aligned}$$

### Grandcanonical potential

grandcanonical potential:

$$\begin{aligned} \Psi(T,V,\mu) &= -k_B T \ln(\Xi_\mu(T,V)) \\ p \text{ is maximal, if } \Psi \text{ is minimal.} \\ \text{Total differential:} \\ d\Psi &= -SdT - pdV - \langle N \rangle d\mu \end{aligned}$$

### Equations of state:

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

### Fluctuations

$$\begin{aligned} \sigma_N^2 &= \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2} \left( \partial_\mu^2 \ln(\Xi_\mu) \right) \\ \frac{\sigma_N}{\langle N \rangle} &\propto \frac{1}{\sqrt{N}} \end{aligned}$$

### Ideal gas

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

### Molecular adsorption onto a surface

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

**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  $\epsilon$

$$\begin{aligned} Z_F &= e^{-\beta\epsilon} \quad \text{Fermi-Dirac} \\ Z_B &= 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} \quad \text{Bose-Einstein} \\ Z_M &= \frac{1 + 2e^{-\beta\epsilon} + e^{-2\beta\epsilon}}{2} \quad \text{Maxwell-Boltzmann} \end{aligned}$$

### Grand canonical ensemble

Fermions:

$$\begin{aligned} z_F &= 1 + e^{-\beta(\epsilon - \mu)} \\ \text{average occupation number } n_F: \\ n_F &= \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \quad \text{Fermi function} \end{aligned}$$

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

$$\begin{aligned} n_F &= \Theta(\mu - \epsilon) \\ \text{Bosons:} \\ z_B &= \frac{1}{1 - e^{-\beta(\epsilon - \mu)}} \end{aligned}$$

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:

$$D(\epsilon) = \frac{V}{2\pi N} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{\epsilon}$$

### Fermi energy

$$\begin{aligned} N &= \sum_{\vec{k}, m_s} n_{\vec{k}, m_s} = N \int_0^\infty d\epsilon D(\epsilon) n_F(\epsilon) \\ \text{Limit } T \rightarrow 0. \mu(T=0) \text{ is called Fermi energy:} \\ \epsilon_F &= (3\pi^2)^{\frac{2}{3}} \frac{\hbar^2 \rho^{\frac{2}{3}}}{2m} \end{aligned}$$

### specific heat

$$\begin{aligned} \mu &= \epsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{\epsilon_F} \right)^2 \right] \text{ for } T \ll \frac{\epsilon_F}{k_B} \\ c_V &= \frac{\partial E}{\partial T} \Big|_V = N \frac{\pi^2}{3} k_B^2 D(\epsilon_F) T \\ c_V &= N \frac{\pi^2}{2} \frac{k_B T}{\epsilon_F} k_B \end{aligned}$$

### Fermi pressure

$$p \xrightarrow{T \rightarrow 0} \frac{2}{5} \frac{N}{V} \epsilon_F = \frac{(2\pi^2)^{\frac{2}{3}}}{5} \frac{\hbar^2}{m v^{\frac{5}{3}}}$$

### The ideal Bose fluid

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

$$\begin{aligned} N &= \frac{N}{\lambda^3} g_{\frac{3}{2}}(z) \\ z &= e^{\beta\mu}, \quad \lambda = \frac{h}{(2\pi m k_B T)^{\frac{1}{2}}} \\ T_c &= \frac{2\pi}{\left( \zeta\left(\frac{3}{2}\right) \right)^{\frac{2}{3}}} \frac{\hbar^2 \rho^{\frac{2}{3}}}{k_B m} \end{aligned}$$

$$\begin{aligned} E &= \frac{3}{2} k_B T \frac{V}{\lambda^3} g_{\frac{5}{2}}(z) = \frac{3}{2} k_B T N e^{\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)}} \\ c_V &= \frac{15}{4} k_B N \left( \frac{T}{T_c} \right)^{\frac{3}{2}} \frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} \quad (\text{for } T \leq T_c) \\ c_V &= \frac{15}{4} k_B N \frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} - \frac{9}{4} k_B N \frac{g_{\frac{3}{2}}(z)}{g_{\frac{1}{2}}(z)} \quad (T > T_c) \end{aligned}$$

**Classical limit**  
 $\mu \rightarrow -\infty$  the two grandcanonical distr. become the Maxwell-Boltzmann distr.

$$\begin{aligned} n_{F/B} &= \frac{1}{e^{\beta(\epsilon - \mu)} \pm 1} \rightarrow e^{\beta\mu} e^{-\beta\epsilon} \\ N &= g \frac{V}{\lambda^3} e^{\beta\mu} \\ E &= \frac{3}{2} k_B T N \end{aligned}$$

### 6 Phase transitions

**Ising model**  
**Hamiltonian**

$$\mathcal{H} = - \sum_{i,j} J_{ij} S_i S_j - \mu B_0 \sum_i S_i$$

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

### 1. Dimensional

Only Next Neighbor and  $B_0 = 0$   
 $J_{i,i+1} \rightarrow J_i, \quad \mathcal{H} = - \sum_{i=1}^{N-1} J_i S_i S_{i+1}, \quad J_i = \beta J_i$

$$\begin{aligned} Z_N &= \sum_{S_1} \dots \sum_{S_N} \exp \left( \sum_{i=1}^{N-1} J_i S_i S_{i+1} \right) \\ &= 2^N \prod_{i=1}^{N-1} \cosh(\beta J_i) \end{aligned}$$

Spin correlation function:

$$\langle S_i S_{i+1} \rangle = \tanh(\beta J)$$

spontaneous magnetisation:

$$\begin{aligned} M_S(T) &= \mu \langle S \rangle \\ M_S^2(T) &= \mu^2 \lim_{j \rightarrow \infty} \langle S_i S_{i+1} \rangle \end{aligned}$$

No phase transition for  $T > 0$ . But for  $T = 0$   
 $M_S(T=0) = \mu$

### Transfer matrix

$$\begin{aligned} j &= \beta J, \quad b = \beta \mu B_0, \quad S_i = \pm 1 \\ T_{i,i+1} &= e^{j S_i S_{i+1} + \frac{1}{2} b (S_i + S_{i+1})} \\ \rightarrow e^{-\beta \mathcal{H}} &= T_{1,2} \cdot T_{2,3} \dots T_{N,1} \\ T &= \begin{pmatrix} T(+1,+1) & T(+1,-1) \\ T(-1,+1) & T(-1,-1) \end{pmatrix} \\ Z_N &= \lambda_1^N + \lambda_2^N = E_+^N + E_-^N \end{aligned}$$

for  $N \gg 1 \rightarrow E_+ \gg E_-$

### Renormalization of the Ising chain

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

### Renormalization of the 2d Ising model

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

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

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

Mean field theory for the Ising model

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j$$
$$\mathcal{H}_0 = -B \sum_i S_i$$
$$F_0 = -N k_B T \ln \left( e^{\beta B} + e^{-\beta B} \right)$$
$$= -N k_B T \ln (2 \cosh(\beta B))$$
$$F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$$
$$= -N k_B T \ln (2 \cosh(\beta B)) - N \frac{z}{2} \langle S \rangle_0^2$$
$$+ N \langle S \rangle_0 = F_u$$
$$\rightarrow z = 2 \cdot \text{dimension}$$
$$B = J z \langle S \rangle_0 = J z \tanh(\beta B)$$

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

7 Classical fluids

Virial expansion

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

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

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