Theoretical Statistical Physics (MKTP1)
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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

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

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

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

Equilibrium conditions

Thermal contact

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

Contact with volume excahnge

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

Contact with exchange of particle number

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

Equations of state

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

Equations of state fo ideal gas

$$S = k_BN\left[\ln\left(\frac{V}{N\lambda^3}\right) + \frac{5}{2}\right] \text{ fundamental}$$
$$E = \frac{3}{2}Nk_BT \qquad \text{caloric}$$
$$pV = Nk_BT \qquad \text{thermal}$$
$$\mu = k_BT\ln\left(\frac{N\lambda^3}{V}\right) \text{ chemical potentail}$$

Einstein model for specific heat of a solid

$$E = \hbar\omega\left(\frac{N}{2} + Q\right)$$
$$\Omega(E,N) = \frac{(Q+N)!}{Q!N!}$$
$$S = k_B\ln(\Omega)$$
$$= k_B\left[Q\ln\left(\frac{Q+N}{Q}\right) + N\ln\left(\frac{Q+N}{N}\right)\right]$$
$$= k_BN\left[(e+\frac{1}{2})\ln(e+\frac{1}{2}) - (e-\frac{1}{2})\ln(e-\frac{1}{2})\right]$$
$$e = E/E_0\ ; E_0 = N\hbar\omega$$
$$\to E = N\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta}-1}\right)$$

Entropic elasticity of polymers

$$N_+ - N_- = \frac{L}{a}$$
$$N_+ = \frac{1}{2}\left(N + \frac{L}{a}\right)$$
$$\Omega = \frac{N!}{N_+!N_-!}$$
$$S = -k_B\left(N_+\ln\left(\frac{N_+}{N}\right) + N_-\ln\left(\frac{N_-}{N}\right)\right)$$

Statistical deviation from average

Two ideal gases in thermal conact $T_1 = T_2$

$$S_i = \frac{3}{2}k_BN_i\ln(E_i) + \text{independent of} E_i$$
$$S = S_1 + S_2$$
$$dS = 0 \to \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$
$$\to \overline{E}_1 = \frac{N_1}{N}E$$

consider small deviation:

$$E_1 = \overline{E}_1 + \Delta E, \quad E_2 = \overline{E}_2 - \Delta E$$
$$S(\overline{E}_1 + \Delta E) \approx \frac{3}{2}k_B\left[N_1\ln\overline{E}_1 + N_2\ln\overline{E}_2 - \frac{N_1}{2}\left(\frac{\Delta E}{\overline{E}_1}\right)^2 - \frac{N_2}{2}\left(\frac{\Delta E}{\overline{E}_2}\right)^2\right]$$
$$\to \Omega = \overline{\Omega}e^{\left[-\frac{3}{4}\left(\frac{\Delta E}{E}\right)^2N^2\left(\frac{1}{N_1}+\frac{1}{N_2}\right)\right]}$$

3 The canonical ensemble

Boltzmann distribution

Temperature T is fixed.

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

For classical Hamiltonian systems:

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

Free energy

probability that the system has energy E

$$p(E) = \frac{1}{Z}\Omega(E)e^{-\beta E} = \frac{1}{Z}e^{-\beta E + S(E)/k_B}$$
$$= \frac{1}{Z}e^{-\frac{E-TS}{k_BT}} = \frac{1}{Z}e^{-\beta F}$$

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 corresponds 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

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

how to calculate F:

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

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

$$\langle E\rangle = \sum_i p_iE_i = \frac{1}{Z}\sum_i E_ie^{-\beta E_i}$$
$$= -\partial_\beta\ln(Z(\beta))$$

Non-interacting systems

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

$$Z = \sum_{j_1}\sum_{j_2}\dots\sum_{j_N} e^{-\beta\sum_{i=1}^N\epsilon_{ij_i}}$$
$$= \left(\sum_{j_1} e^{-\beta\epsilon_{1j_1}}\right)\dots\left(\sum_{j_N} e^{-\beta\epsilon_{Nj_1N}}\right)$$
$$= z_1\cdot\dots\cdot z_N = \prod_{i=1}^N z_i$$
$$\to F = -k_BT\sum_{i=1}^N\ln(z_i) = -k_BT\ln(Z)$$
$$Z = z^N, \qquad F = -k_BTNln(z)$$

TODO: ADD EXAMPLES

Equipartition theorem

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

$$\mathcal{H} = Aq^2 + Bp^2$$
$$z \propto \int dqdpe^{-\beta\mathcal{H}}$$
$$= \left(\frac{\pi}{A\beta}\right)^{\frac{1}{2}}\cdot\left(\frac{\pi}{B\beta}\right)^{\frac{1}{2}}$$
$$\propto \left(T^{\frac{1}{2}}\right)^f$$

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'**)

$$F = -k_BT\ln(z) = -\frac{f}{2}k_BTln(T)$$
$$S = -\frac{\partial F}{\partial T} = \frac{f}{2}k_B(\ln(T)+1)$$
$$U = -\partial_\beta\ln(z) = \frac{f}{2}k_BT$$
$$c_v = \frac{dU}{dT} = \frac{f}{2}k_B$$

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:

$$z_{vib} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega_0}}$$
$$T_{vib} \approx \frac{\hbar\omega_0}{k_B} \approx 6.140K \text{ for } H_2$$

Rotational modes

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

$$I = \mu r_0^2 \quad T_{rot} = \frac{\hbar^2}{Ik_B}$$
$$\to E_l = \frac{\hbar^2}{2I}l(l+1)$$

Nuclear contributions: ortho- and parahydrogen

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

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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 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:

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

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

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

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

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

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:

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

4 The grandcanonical ensemble

Probability distribution

T and μ are fixed.

$$p_i = \frac{1}{Z_G}e^{-\beta(E_i-\mu N_i)} \text{ prob. distribution}$$
$$Z_G = \sum_i e^{-\beta(E_i-\mu N_i)} \text{ partition sum}$$
$$\Psi = -k_B T\ln(Z_G) \text{ thermodynamic potential}$$

Grandcanonical potential

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

$$p(E,N) = \frac{1}{Z_G}\Omega(E,N)e^{-\beta(E-\mu N)}$$
$$= \frac{1}{Z_G}e^{-\beta(E-TS-\mu N)} = \frac{1}{Z_G}e^{-\beta\Psi(T,V,\mu)}$$

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

$$Z(T,V,N) = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N, \ \lambda = \frac{h}{(2\pi mk_B T)^{\frac{1}{2}}}$$
$$Z_G = \sum_{N=0}^{\infty} Z(T,V,N)e^{\beta\mu N}$$
$$= \sum_{N=0}^{\infty}\frac{1}{N!}\left(e^{\beta\mu}\frac{V}{\lambda^3}\right)^N$$
$$= e^{z\frac{V}{\lambda^3}} \quad \text{fugacity: } z := e^{\beta\mu}$$
$$\langle N\rangle = \frac{1}{\beta}\partial_\mu\ln(Z_G) = \frac{V}{\lambda^3}e^{\beta\mu}$$
$$\mu = k_B T\ln\left(\frac{N\lambda^3}{V}\right)$$

Molecular adsorption onto a surface

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

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

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

Grand canonical ensemble

Fermions:

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

average occupation number n_F:

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

For $T\to 0$, 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:

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

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 $T\to 0$. $\mu(T=0)$ 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

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

The ideal Bose fluid

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

$$N = \frac{N}{\lambda^3}g_{\frac{3}{2}}(z)$$
$$z = e^{\beta\mu}, \ \lambda = \frac{h}{(2\pi mk_B T)^{\frac{1}{2}}}$$
$$T_c = \frac{2\pi}{\left(\zeta\left(\frac{3}{2}\right)\right)^{\frac{3}{2}}}\frac{\hbar^2\rho^{\frac{2}{3}}}{k_B m}$$
$$E = \frac{3}{2}k_B T\frac{V}{\lambda^3}g_{\frac{5}{2}}(z) = \frac{3}{2}k_B TN_e\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)}$$
$$c_V = \frac{15}{4}k_B N\left(\frac{T}{T_c}\right)^{\frac{3}{2}}\frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} \text{ (for } T \le T_c)$$
$$c_V = \frac{15}{4}k_B N\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} - \frac{9}{4}k_B N\frac{g_{\frac{3}{2}}(z)}{g_{\frac{1}{2}}(z)} \ (T > T_c)$$

Classical limit

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

$$n_{F/B} = \frac{1}{e^{\beta(\epsilon-\mu)}\pm 1} \to e^{\beta\mu}e^{-\beta\epsilon}$$
$$N = g\frac{V}{\lambda^3}e^{\beta\mu}$$
$$E = \frac{3}{2}k_B TN$$

6 Phase transitions

Ising model

$$\mathcal{H} = -J\sum_{\langle ij\rangle}S_i S_j - B\mu\sum_i S_i$$
$$\beta\mathcal{H} = -K\sum_{\langle ij\rangle}S_i S_j - H\sum_i S_i$$
$$K = \beta J, \quad H = \beta B\mu$$
$$Z_N(K,H) = \sum_{S_1=\pm1}\dots\sum_{S_N=\pm1}e^{-\beta\mathcal{H}}$$

The 1D Ising model

$$Z_N \overset{N\gg1}{\approx} (2\cosh(K))^N$$
$$F = -k_B TN\ln\left(2\cosh\left(\frac{J}{k_B T}\right)\right)$$
$$\forall i: K_i = K \Rightarrow (\tanh(K))^j$$

7 Others

Stirling's formula

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

de Broglie relation

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