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**

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

**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 $T_1 = T_2$

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

consider small deviation:

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

# 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 $F$:

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

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**

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

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

**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:

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

**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:

$$\omega_D = c_s \left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$$
$$c_s = \frac{d\omega}{dk}\bigg|_{k=0} = \sqrt{\frac{\kappa}{m}}a$$

density of states in $\omega$−space:

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

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:

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

## 4 The grandcanonical ensemble

**Probability distribution**
$T$ and $\mu$ 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 $\Psi$ 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**

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

**Molecular adsorption onto a surface**

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

## 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.

## 6 Others

**Stirling's formula**

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