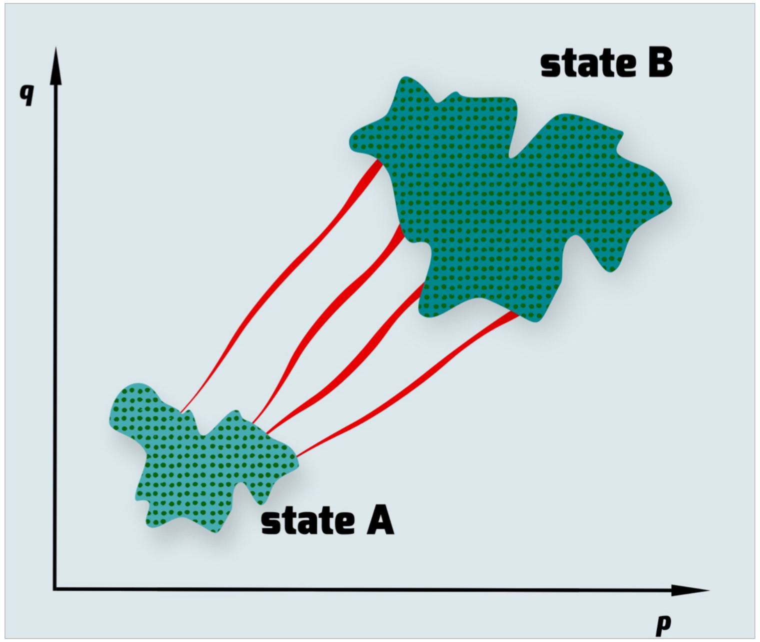
Lecture 6
30.01.2019

recap of module I

Module I: Thermodynamics (review) and statistical ensembles

ti. 15. jan.	Introduction/Thermodynamics laws, entropy
on. 16. jan.	Thermodynamic potentials, response functions and Maxwell’s relations, thermodynamic stability
ti. 22. jan.	Statistical ensembles, Phase space, Liouville’s theorem, microcanonical ensemble
on. 23. jan.	Canonical ensemble
ti. 29. jan.	Grand-canonical ensemble

Ensemble density of states



- Phase space (p, q) – $2\text{d}\times N$ dim. space
- Representative volume element

$$d\omega = \frac{d^{dN}p\, d^{dN}q}{(2\pi\hbar)^{dN}} \equiv \#$$ of **microstates** in a unit volume

- Ensemble Probability density $\rho(p, q)$: is the probability that **a particular microstate** is occupied by the system
- Liouville's theorem for equilibrium ensembles $\{\boldsymbol{\rho}, \boldsymbol{H}\} = \mathbf{0} \rightarrow \boldsymbol{\rho}(\boldsymbol{p}, \boldsymbol{q}) = \boldsymbol{\rho}(\boldsymbol{H}(\boldsymbol{p}, \boldsymbol{q}))$

Microcanonical Ensembles: equilibrium of isolated systems

Equilibrium ensemble density of states: $\boldsymbol{\rho(p,q) = \frac{1}{\Sigma(U)}\ \delta(H(p,q) - U)}$

- Microcanonical density of states: $\boldsymbol{\Sigma(U,V,N) = \int d\omega\, \delta(H(p,q) - U)}, \mathrm{d}\omega = \frac{d^{3N}p d^{3N}q}{(2\pi\hbar)^{3N}}$

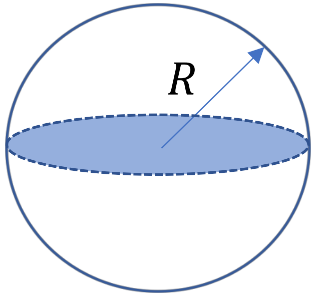
- Describes a system at a fixed energy, volume and number of particles
- **Each possible state at fixed U and N has an equal probability**

- Phase space volume: $\boldsymbol{\Omega(U,V,N) = \int_{H(p,q)\leq U} d\omega\ \ \delta(H(p,q) - U)}$

- Boltzmann's formula (correspondence to thermodynamics)

Entropy: $\mathbf{S(U,V,N) = k\ ln\ [\Omega(\mathit{U},\mathit{V},\mathit{N})]}$

Microcanonical ensemble: Ideal gas



Microcanonical phase space volume of free particles

$$\Omega(U,N) = \frac{1}{N!}\frac{V^N}{(2\pi\hbar)^{3N}}\frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}(2mU)^{\frac{3N}{2}}, \qquad \Sigma(U) = \frac{\partial\Omega(U)}{\partial U}$$

Boltzmann's formula

$$S(U,N) = k\ln\Omega(U,N) = \boldsymbol{kN\left\{\frac{5}{2} + \ln\frac{V}{N}\left(\frac{mU}{3\pi N\hbar^2}\right)^{\frac{3}{2}}\right\}}$$

$$\boldsymbol{dS = \frac{1}{T}dU + \frac{P}{T}dV + \mu dN}$$

- *Temperature* $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{3Nk}{2}\frac{1}{U} \rightarrow U = \frac{3}{2}NkT$
- *Pressure* $\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{Nk}{V} \rightarrow PV = NkT$

Canonical Ensembles: equilibrium with a thermal bath

- Describes a system that is in thermal equilibrium with a heat bath at **a fixed temperature T** in terms of the equilibrium density

$$\boldsymbol{\rho(p,q) = \frac{1}{Z(T)} e^{-\beta H(p,q)}, \qquad \int d\omega\, \rho(p,q,n) = 1}$$

- Canonical partition function and **Helmholtz free energy (thermodynamics correspondence)**

$$\boldsymbol{Z(T) = \int d\omega e^{-\beta H(p,q)} = e^{-\beta F(T)}}$$

- Energy fluctuates around the average, equilibrium value $U = \langle E \rangle$, with a probability $P(E) = \frac{1}{Z} e^{-\beta(E-TS)}$

$$\boldsymbol{Z(T,V) = \int dE\, e^{-\beta E} \Sigma(E) = e^{-\beta F(T)}, \qquad F = U - TS(U), \qquad \langle E \rangle = U = -\frac{\partial}{\partial \beta} \ln Z(T)}$$

- Energy Fluctuations

$$\langle \Delta E^2 \rangle = \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z - \left(\frac{1}{Z} \frac{\partial}{\partial \beta} Z \right)^2 = \frac{\partial^2}{\partial \beta^2} \ln Z$$

Fluctuations are much smaller than the average in the thermodynamic limit: $\boldsymbol{\frac{\sqrt{\langle \Delta E^2 \rangle}}{\langle E \rangle} \sim \frac{1}{\sqrt{N}} \to 0}$

Canonical ensemble: Ideal gas

$$Z_N(T,V) = \frac{1}{N!}\frac{V^N}{\Lambda^{3N}(T)} = \frac{1}{\text{N!}} Z_1^N, \quad \Lambda = \frac{h}{\sqrt{2\pi m k T}}$$

Thermodynamic correspondence

$$F(T,V,N) = -kT \ln \text{Z}_N(T,V) = -\, NkT \left[\ln\left(\frac{V}{N\Lambda^3(T)}\right) + 1\right],$$

$$dF = -SdT - PdV + \mu dN$$

- $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk[\ln\left(\frac{V}{N\Lambda^3(T)} + 1\right) + \frac{3N}{2}k = \frac{-F+U}{T}$
- $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V}$
- $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT \ln\left(\frac{V}{N\Lambda^3(T)}\right) \to \frac{V}{N\Lambda^3(T)} = e^{-\beta\mu}$

Energy fluctuations for a macrostate at fixed T: $P(E) = \frac{\Sigma(E)}{Z(T)}\, e^{-\beta E} \sim \frac{E^{3N}}{N!}\, e^{-\beta E}$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\log Z = -\frac{3N}{2}\frac{\partial}{\partial\beta}\log\frac{2\pi m}{\beta} = \frac{3N}{2}kT \sim N$$

$$\langle \Delta E^2\rangle = \frac{\partial^2}{\partial\beta^2}\log Z = -\frac{3N}{2}\frac{\partial}{\partial\beta}\frac{1}{\beta} = \frac{3N}{2}k^2T^2 \sim N$$

Grand-Canonical Ensembles: equilibrium with a particle and thermal reservoir

- Describes a system that is in thermal and chemical equilibrium with a reservoir at **a fixed temperature T and chemical potential μ**

$$\boldsymbol{\rho(p,q,n) = \frac{1}{\Sigma(T,\mu)}\frac{1}{n!}e^{-\beta[H(p,q)-\mu n]}}, \qquad \boldsymbol{\sum_n \int d\omega\, \rho(p,q,n) = 1}$$

- Grand Canonical partition function and **Landau free energy (thermodynamics correspondence)**

$$\Xi(T,\mu) = \sum_{n=0}^{\infty}\frac{e^{\beta\mu n}}{n!}\int d\omega\, e^{-\beta H(p,q)} = \boldsymbol{\sum_{n=0}^{\infty} e^{-\beta(F-\mu n)} = e^{-\beta\Omega(T,\mu)}}, \qquad \boldsymbol{\Omega(T,\mu) = F(T,N) - \mu N}$$

- Particle number fluctuates around the average, equilibrium value

  $N = \langle n \rangle$, with a probability $P(n) = \frac{1}{\Sigma(T,\mu)} e^{-\beta(F-\mu n)}$, $\boldsymbol{\sum_n P(n) = 1}$

$$\boldsymbol{\langle n \rangle = N = kT\frac{\partial}{\partial\mu}\, ln\, \Sigma(T,\mu)}$$

- Particle number fluctuations

$$\langle \Delta n^2 \rangle = (kT)^2 \frac{\partial^2}{\partial\mu^2}\ln\Sigma(T,\mu)$$

Grand-Canonical ensemble: Ideal gas

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

- $\Xi(T,V,\mu) = \sum_{n=0}^{\infty} \frac{1}{n!}\left(\frac{V}{\Lambda^3} e^{\beta\mu}\right)^n = e^{z(T,\mu)V}$, $z = \frac{e^{\beta\mu}}{\Lambda^3(T)}$ is the **fugacity**

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

- Thermodynamic correspondence: Landau potential

$$\Omega(T,\mu) = -kT\,zV = -kTV\frac{e^{\beta\mu}}{\Lambda^3(T)}, \qquad d\Omega = -SdT - PdV - Nd\mu$$

- Number fluctuations $P(n) \sim \frac{1}{n!}\frac{V^n}{\Lambda^{3n}} e^{\beta\mu n}$

$$\langle \Delta n^2 \rangle = (kT)^2 \frac{\partial^2}{\partial\mu^2} \ln \Xi = V\frac{e^{\beta\mu}}{\Lambda^3(T)}$$

$$\langle n \rangle = kT\frac{\partial}{\partial\mu}\ln\Xi = V\frac{e^{\beta\mu}}{\Lambda^3(T)}$$

Monte Carlo algorithm

- Evaluate multivariable integrals by random sampling from a known equilibrium distribution (e.g. canonical ensemble distribution—Boltzmann statistics)

$$\langle \boldsymbol{E}\rangle(\boldsymbol{T}) = \frac{\mathbf{1}}{(\mathbf{2}\boldsymbol{\pi}\hbar)^{\mathbf{3N}}}\frac{\int \boldsymbol{d}^{\mathbf{3N}}\boldsymbol{p}\boldsymbol{d}^{\mathbf{3N}}\boldsymbol{q}\ \boldsymbol{E}(\boldsymbol{p},\boldsymbol{q})\boldsymbol{e}^{-\ \boldsymbol{\beta}\boldsymbol{E}(\boldsymbol{p},\boldsymbol{q})}}{\boldsymbol{Z}(\boldsymbol{T})}$$

- The goal of a simulation is sampling through a large enough subset of the microstates of the equilibrium ensemble, so that averages of observables (e.g. energy) approach their equilibrium values.
- After a simulation has run long enough for the system to approach equilibrium, the simulation then generates a sequence of M configurations, $\{q_j\}_{j=1}^{M}$ chosen from the set of microstates in the equilibrium ensemble and the corresponding sequence for the value of the energy in each microstate, $\{E(q_j)\}_{j=1}^{M}$
- At equilibrium, the microstates are drawn from the canonical density of states $\boldsymbol{P}_{\boldsymbol{eq}}(\boldsymbol{q}) = \frac{\boldsymbol{e}^{-\ \boldsymbol{\beta}\boldsymbol{E}(\boldsymbol{q})}}{\sum_{\{\boldsymbol{q}'\}}\boldsymbol{e}^{-\boldsymbol{\beta}\boldsymbol{E}(\boldsymbol{q}')}}$
- $\langle \boldsymbol{E}\rangle = \langle \boldsymbol{E}\rangle_{\boldsymbol{M}} \pm \boldsymbol{\sigma}_{\boldsymbol{M}}$

$$\langle \boldsymbol{E}\rangle_{\boldsymbol{M}} = \frac{\mathbf{1}}{\boldsymbol{M}}\sum_{\boldsymbol{j}=\mathbf{1}}^{\boldsymbol{M}}\boldsymbol{E}(\boldsymbol{q}_{\boldsymbol{j}}), \qquad \boldsymbol{\sigma}_{\boldsymbol{M}}^{\mathbf{2}} = \langle \boldsymbol{E}^{\mathbf{2}}\rangle_{\boldsymbol{M}} - \langle \boldsymbol{E}\rangle_{\boldsymbol{M}}^{\mathbf{2}} = \frac{\mathbf{1}}{\boldsymbol{M}}\sum_{\boldsymbol{j}=\mathbf{1}}^{\boldsymbol{M}}\left[\boldsymbol{E}(\boldsymbol{q}_{\boldsymbol{j}}) - \langle \boldsymbol{E}\rangle_{\boldsymbol{M}}\right]^{\mathbf{2}}$$

Metropolis Monte Carlo algorithm

- Equilibrium condition for the ensemble density

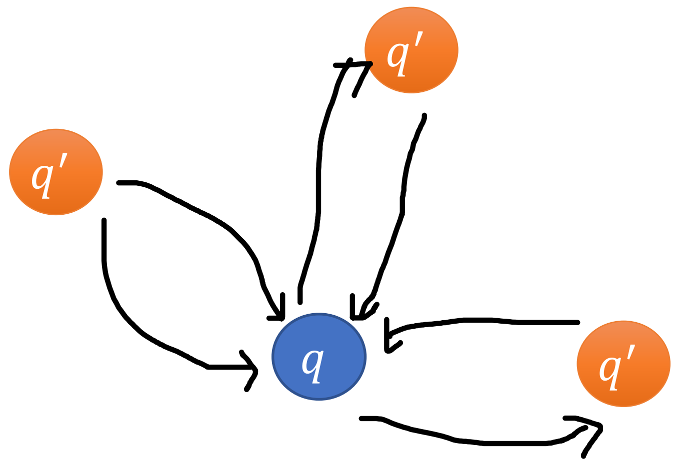
$$\sum_{q'} P_{eq}(q')\, W(q' \to q) = P_{eq}(q) \sum_{q'} W(q \to q')$$

- Detailed balance condition (stronger constraint)

$$\frac{P_{eq}(q')}{P_{eq}(q)} = \frac{W(q \to q')}{W(q' \to q)} \to e^{-\beta \Delta \mathrm{E}} = \frac{W(q \to q')}{W(q' \to q)}$$

- Metropolis rule for the transition probability

$$W(q \to q') = \begin{cases} 1, & \Delta \mathrm{E} \leq 0 \\ e^{-\beta \Delta E}, & \Delta E > 0 \end{cases}$$



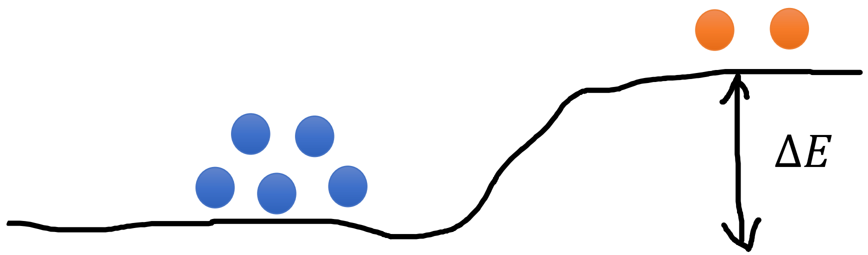
Metropolis Monte Carlo : Ideal gas

- Detailed balance: $\frac{P_{eq}(v\prime)}{P_{eq}(v)} = \frac{W(v \to v')}{W(v' \to v)} = e^{-\beta\Delta E}$, $E = \frac{1}{2}mv^2$

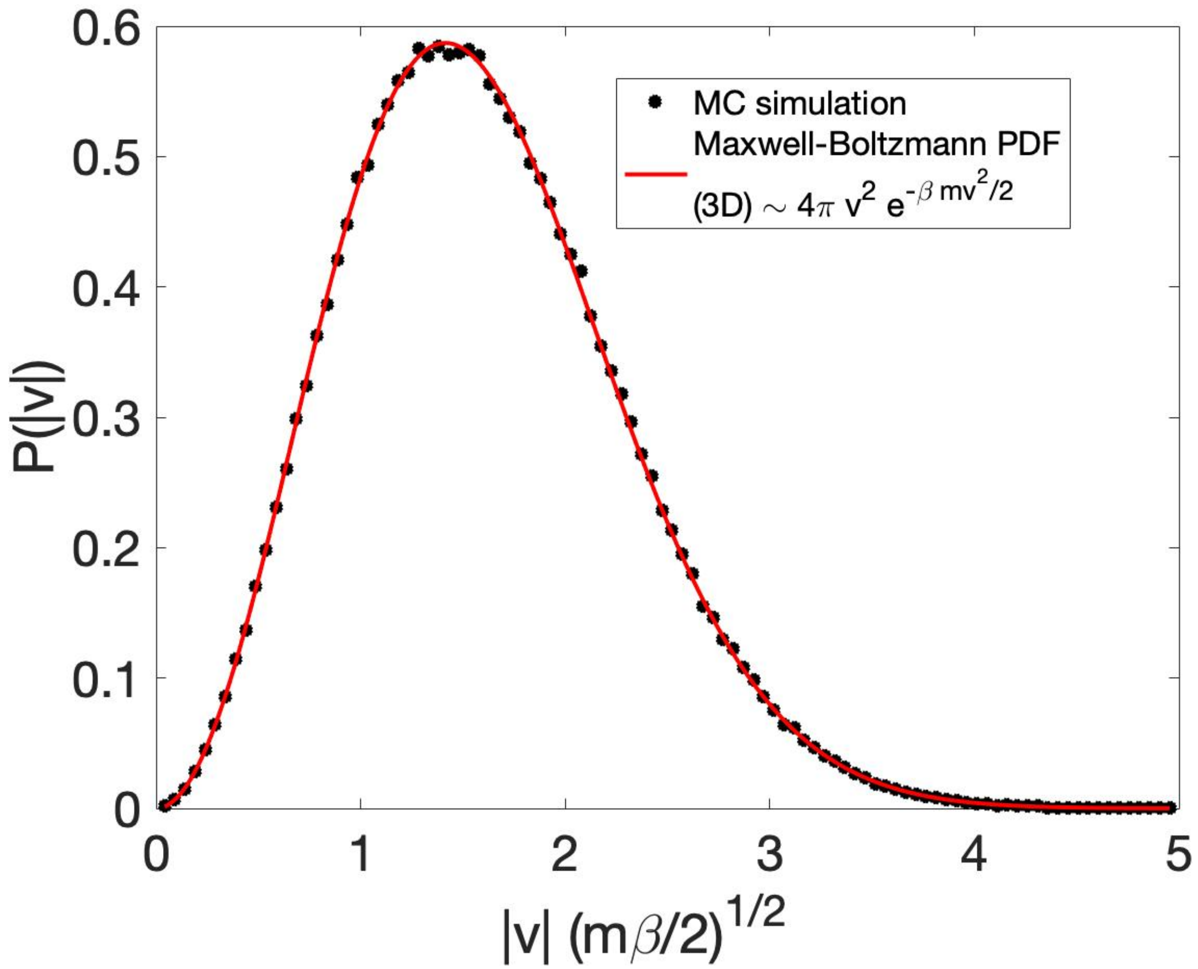
Metropolis rule for the transition probability

$$W(v \to v') = \begin{cases} 1, & \Delta E \leq 0 \\ e^{-\beta\Delta E}, & \Delta E > 0 \end{cases}$$

- $v^{new} = v^{old} + s(2\,rand(\quad) - 1)$
- If $E^{new} \leq E^{old}$, accept the move
- If $E^{new} > E^{old}$, accept the move with $e^{-\beta\Delta E}$



Metropolis Monte Carlo : Ideal gas

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% for each trial generate a new velocity
vnew = v+s*(2*rand(size(v))-1);
% estimate the energy change
DE   = m/2*sum(vnew.^2-v.^2);
% estimate the jump probability
W    = exp(-beta*DE);
r    = rand;
% accept the move if it lowers the energy or if the jump
probability is larger than a random nr in [0,1]
v    = vnew.*(DE<=0)+...
       (DE>0).*(vnew*(r<=W)+v.*(r>W));
% collect particle speed for the accepted microstate
V(n)=norm(v);
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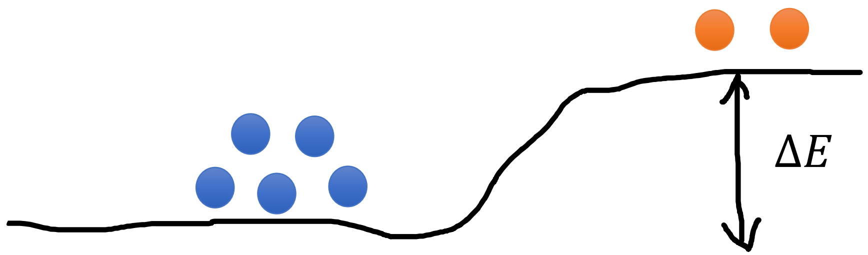

Metropolis Monte Carlo : Ideal gas