Compressibility and fluctuations

Grandcanonical partition function in semiclassical approximation:

$$-k_BT\ln Z_{\mu VT}=F-\mu\langle N\rangle=\Omega=-pV,\quad\text{where } Z_{\mu VT}=\sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{N!h^{3N}}\int e^{-\beta E}d\vec r_1\dots\dots d\vec p_N$$

System of N identical particles in the grandcanonical ensemble (μVT), μ = parameter

$$\langle N\rangle=-\left(\frac{\partial\Omega}{\partial\mu}\right)_{V,T}=\frac{\sum_{N=0}^{\infty}N\frac{e^{\beta\mu N}}{\Lambda^{3N}N!}\int e^{-\beta E}d\vec r_1\dots d\vec p_N}{\sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{\Lambda^{3N}N!}\int e^{-\beta E}d\vec r_1\dots d\vec p_N}=\frac{\sum_{N=0}^{\infty}N\frac{e^{\beta\mu N}}{N!\Lambda^{3N}}Q_N}{\sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{N!\Lambda^{3N}}Q_N},$$

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{V,T}=\beta\frac{\sum_{N=0}^{\infty}N^2\frac{e^{\beta\mu N}}{N!\Lambda^{3N}}Q_N\times\sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{N!\Lambda^{3N}}Q_N-\sum_{N=0}^{\infty}N\frac{e^{\beta\mu N}}{N!\Lambda^{3N}}Q_N\times\sum_{N=0}^{\infty}N\frac{e^{\beta\mu N}}{N!\Lambda^{3N}}Q_N}{\left(\sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{N!\Lambda^{3N}}Q_N\right)^2}$$

$$=\beta\left(\langle N^2\rangle-\langle N\rangle^2\right)=\beta\langle(N-\langle N\rangle)^2\rangle=\beta\,\mathrm{Var}\,N$$

Compressibility and fluctuations

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{V,T}=\beta\,\mathrm{Var}\,N$$

Grandcanonical potential: $\Omega=F-N\mu=-pV=-\beta\ln Z_{\mu VT}$ $\qquad dF=-SdT-pdV+\mu dN$

Differential: $d\Omega=-pdV-Vdp=-SdT-pdV-Nd\mu\ \Rightarrow\ Nd\mu=Vdp\ \ [T,N,V]$
Another derivation: $dG=Nd\mu=Vdp\ \ [T,N]$

p and μ are intensive variables, hence they depend on $\rho=\langle N\rangle/V$ only:

$$N\left(\frac{\partial\mu}{\partial N}\right)_{T,V}=V\left(\frac{\partial p}{\partial N}\right)_{T,V}=\left(\frac{\partial p}{\partial(N/V)}\right)_T=\frac{1}{N}\left(\frac{\partial p}{\partial(1/V)}\right)_{T,N}=\frac{V}{N}\left[-V\left(\frac{\partial p}{\partial V}\right)_{T,N}\right]=\frac{1}{\rho\kappa_T}$$

Eventually:

$$\frac{\mathrm{Var}\,N}{\langle N\rangle}=\rho k_BT\kappa_T$$

isothermal compressibility:

$$\kappa_T=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}$$

bulk modulus:

$$B_T=1/\kappa_T$$

Compressibility and fluctuations

$$\frac{\mathrm{Var}\,N}{\langle N\rangle}=\rho k_BT\kappa_T$$

- larger compressibility ⇒ larger fluctuations
- $\mathrm{Var}\,N>0\Rightarrow\kappa_T>0$ ($\kappa_T<0$ for a mechanically unstable system)
- $\mathrm{Var}\,\rho=\frac{\rho^3k_BT\kappa_T}{N}\overset{N\to\infty}{=}0$ (thermodynamic limit)

typical "finite-size effect" is $\mathcal{O}(1/N)$

Exceptions:

- diffusivity in MD: $\mathcal{O}(1/N^{1/3})$ – a particle interacts with its periodic image $\propto 1/N^{1/3}$ apart
- crystals: $\mathcal{O}(\log N/N)$ – counting phonons
- plasma, ionic solutions (more terms): $\mathcal{O}(1/N^{3/2})$ – Debye–Hückel
- some 2D systems: $\mathcal{O}(\log N/N)$
- critical point – critical exponents

RDF in the μVT ensemble and compressibility

$$\rho^2g(r)=\frac{\sum_{N=2}^{\infty}N(N-1)\frac{e^{\beta\mu N}}{N!\Lambda^{3N}}\int\exp(-\beta U)d\vec r_3\dots d\vec r_N}{\sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{N!\Lambda^{3N}}\int\exp(-\beta U)d\vec r_1\dots d\vec r_N},\qquad r=|\vec r_1-\vec r_2|$$

⇒ **Compressibility equation** $1+\rho\int[g(r)-1]\,d\vec r=\frac{\mathrm{Var}\,N}{\langle N\rangle}=\rho k_BT\kappa_T$ $\qquad$ spherical symmetry: $\int d\vec r=\int_0^\infty 4\pi r^2dr$

- More fluctuation and correlation quantities can be expressed by similar integrals (Kirkwood–Buff)
- Numerically ill-defined for large r – must be cut off
- Tricks to be able to use the NVT ensemble

Exercise 1. Show that $g_{\mu VT}(r)=1$ for monoatomic ideal gas
Hint: for ideal gas $e^{\beta\mu N}/\Lambda^3=p/k_BT=\langle N\rangle/V=\rho$

Exercise 2. Calculate κ_T from the compressibility equation with the canonical RDF (N = constant)

$\kappa_T=0$ – incompressible by definition

Simulation in other ensembles

- NVE → NVT (MD), measuring: $T\to E$
- NVT → NVE (MC), measuring: $E\to T$
- NVT → NPT (MC, MD), measuring: $P\to V$
- NVT → μVT (MC, [MD]), measuring: $\mu\to N$

In the thermodynamic limit ($N\to\infty$) equivalent, otherwise errors $\propto 1/N$*

Corrections:

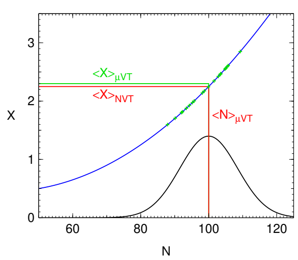
$$\langle X\rangle_{\mu VT}-\langle X\rangle_{NVT}\approx\frac12\left\langle(N-\langle N\rangle_{\mu VT})^2\right\rangle_{\mu VT}\left(\frac{\partial^2\langle X\rangle_{\mu VT}}{\partial N^2}\right)_{V,T},\quad N=\langle N\rangle_{\mu VT}$$

$$=\frac{k_BT}{2N}\left(\frac{\partial\rho}{\partial p}\right)_T\rho^2\left(\frac{\partial^2\langle X\rangle}{\partial\rho^2}\right)_T$$

where $\langle\cdot\rangle$ in the last derivative is either $\langle\cdot\rangle_{\mu VT}$ or $\langle\cdot\rangle_{NPT}$

Derivation: Taylor expansion of $X(N)$ okolo $\langle N\rangle$

The corrections become important near the critical point



* not for: nonperiodic b.c., (surface $N^{2/3}$), crystals ($\ln N/N$), diffusivity ($N^{1/3}$)...

MC in the microcanonical ensemble

MC move under constraint E = const = problem

It is possible in the classical mechanics for $E_{pot}+E_{kin}$ = const: can be integrated over momenta (not so trivial, though).

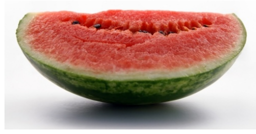
Approximate solution – Creutz

$$E=E_{max}\quad\to\quad E\le E_{max}$$

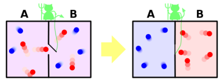
(do not buy a melon in a many-dimensional space)

Creutz demon has a bag with energy: $E_{bag}=E_{max}-E\ge 0$

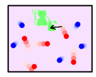
E_{bag} has the Boltzmann distribution ⇒ temperature



Maxwell's demon



Creutz's demon



Credit: Wikipedia (modified)

Creutz – Metropolis comparison

- Choose a particle (lattice site, ...) to move
- $A^{tr}:=A^{(k)}$ + random move of the chosen particle
- $\Delta U:=U(A^{tr})-U(A^{(k)})\equiv U^{tr}-U^{(k)}$
- The configuration is accepted ($A^{(k+1)}:=A^{tr}$) with probability $\min\{1,e^{-\beta\Delta U}\}$ otherwise rejected:

Metropolis	Creutz	Creutz–Metropolis
$u:=u_{(0,1)}$		bag $=-k_BT\ln u_{(0,1)}$
IF $u<e^{-\beta\Delta U}$	IF $\Delta U<$ bag	IF $\Delta U<$ bag
THEN	THEN	THEN
$A^{(k+1)}:=A^{tr}$	$A^{(k+1)}:=A^{tr}$; bag $-=\Delta U$	$A^{(k+1)}:=A^{tr}$; bag $-=\Delta U$
ELSE	ELSE	ELSE
$A^{(k+1)}:=A^{(k)}$	$A^{(k+1)}:=A^{(k)}$	$A^{(k+1)}:=A^{(k)}$

in all cases $\langle\text{bag}\rangle=k_BT$ (in continuous world: $\langle-\ln u_{(0,1)}\rangle=1$)

- $k:=k+1$ and again and again

NPT ensemble in MC

To incorporate volume change, $\langle X\rangle$ must be in the form of an $\int$ of probability density: $\vec r_i=V^{1/3}\vec\xi_i$

$$\langle X\rangle=\frac{1}{Q_{NPT}}\int_0^\infty\left(\int_{V^N}X(\vec r^N,V)\frac{N}{V}\exp\{-\beta[pV+U(\vec r^N)]\}\,d\vec r^N\right)dV$$

$$=\frac{1}{Q_{NPT}}\int_0^\infty\int_{1^{3N}}X(V^{1/3}\vec\xi^N,V)\frac{N}{V}V^N\exp\{-\beta[pV+U(V^{1/3}\vec\xi^N)]\}\,d\vec\xi^NdV$$

N/V, $^{-1}$: exact ideal gas
βp, const: $\mathcal{O}(1/N)$ error

Microreversible volume change: $V^{tr}=V+u_{(-d,d)}$, then

$$p_{acc}=\min\{1,(V^{tr}/V)^{N-1}\exp[-\beta p(V^{tr}-V)]\exp[-\beta(U^{tr}-U)]\}$$

Better option: $V^{tr}=V\exp[u_{(-d,d)}]$ ($\ln V$ is uniformly sampled), then:

$$p_{acc}=\min\{1,(V^{tr}/V)^{N+1-1}\exp[-\beta p(V^{tr}-V)]\exp[-\beta(U^{tr}-U)]\}$$

- Usually N one-particle moves (translations:rotations = 1:1) per one volume-change move
- Acceptance ration of volume changes ∼ 0.3
- General problem: global change of configuration ⇒ slow convergence ⇒ not good for too large systems

Grandcanonical ensemble in MC

- MC step: change the number of particles by ±1 $\qquad \vec r_i=V^{1/3}\vec\xi_i$

$$\langle X\rangle=\frac{1}{\Xi}\sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{\Lambda^{3N}N!}\int X(\vec r^N,N)\exp[-\beta U_N(\vec r^N)]d\vec r^N$$

$d\vec r^N$ depends on N ⇒ dimensionless coordinates $\vec r_i=V^{1/3}\vec\xi_i$

$$\langle X\rangle=\frac{1}{\Xi}\sum_{N=0}^{\infty}\int_{1^{3N}}X(V^{1/3}\vec\xi^N,N)\frac{e^{\beta\mu N}V^N}{\Lambda^{3N}N!}\exp[-\beta U_N(V^{1/3}\vec\xi^N)]\,d\vec\xi^N$$

- Insert or remove a particle with the same probability 1/2

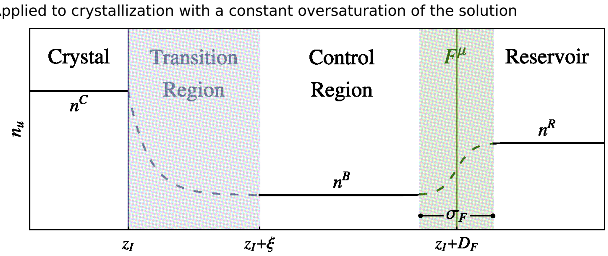
$$p_{\text{insert particle}}=\min\left\{1,\frac{e^{\beta\mu}V}{\Lambda^3(N+1)}\exp\{-\beta[U_{N+1}(\vec r^{N+1,\text{zkus}})-U_N(\vec r^N)]\}\right\}$$

$$p_{\text{remove particle}}=\min\left\{1,\frac{N\Lambda^3}{e^{\beta\mu}V}\exp\{-\beta[U_{N-1}(\vec r^{N-1,\text{zkus}})-U_N(\vec r^N)]\}\right\}$$

Problem: insert a large molecule $\qquad e^{\beta\mu}=\Lambda^3e^{\beta\mu_{res}}\langle N\rangle/V$
Solution: gradually

Grandcanonical ensemble in MD

- The same as in MD, but "continuously" – problematic
- CμMD [Perego, Salvalaglio, Parrinello, DOI: 10.1063/1.4917200]
  - Reservoir with molecules, region with a force ⇒ change of the (chem.) pot.
  - Applied to crystallization with a constant oversaturation of the solution



Reaction ensemble in MC

- We can easily calculate a chemical equilibrium in an ideal gas phase.
  But what if the mixture is not ideal? 1) Calculate μ_i, γ_i... 2) Reaction ensemble

Reaction (reactants: $\nu_i < 0$, products: $\nu_i > 0$): $\sum_{i=1}^{k} \nu_i A_i = 0$

Equilibrium: $$\Delta_\mathrm{r} G_\mathrm{m} = \sum_{i=1}^{k} \nu_i \mu_i = 0$$

Generalized partition function of a mixture, $N = \sum_{i=1}^{k} N_i$ (constant N_i):

$$Z(N_1, \dots, N_k, V, T) = \prod_{i=1}^{k} \frac{(q_i/\Lambda_i^3)^{N_i}}{N_i!} \times \int \exp[-\beta U(\vec{r}^N)] \mathrm{d}\vec{r}^N$$

Balance (extent of reaction = ζ): $N_i = N_i^{(0)} + \zeta \nu_i$

$$Z(N_1^{(0)}, \dots, N_k^{(0)}, V, T) = \sum_{\zeta} \prod_{i=1}^{k} \frac{(V q_i/\Lambda_i^3)^{N_i^{(0)} + \zeta\nu_i}}{(N_i^{(0)} + \zeta\nu_i)!} \times \int \exp[-\beta U(V^{1/3}\vec{\xi}^N)] \mathrm{d}\vec{\xi}^N$$

Reaction ensemble in MC

Reaction "move" $\zeta^\mathrm{tr} = \zeta + \Delta\zeta$ accepted with probalility

$$p_\mathrm{acc} = \min\left\{1, K'^{\Delta\zeta} \exp(-\beta\Delta U) \prod_{i=1}^{k} \left[\frac{(N_i^{(0)} + \zeta\nu_i)!}{(N_i^{(0)} + \zeta^\mathrm{tr}\nu_i)!}\right]\right\}$$

where

$$\Delta U = U(V^{1/3}\vec{\xi}^N, \zeta^\mathrm{tr}) - U(V^{1/3}\vec{\xi}^N, \zeta)$$

$$\bar{\nu} = \sum_{i=1}^{k} \nu_i$$

$$K' = \prod_{i=1}^{k} \left(\frac{V q_i}{\Lambda_i^3}\right)^{\nu_i} = \left(\frac{Vp}{kT}\right)^{\bar{\nu}} \exp\left(-\frac{\sum \mu_{i,\mathrm{id}}}{kT}\right) = \left(\frac{Vp}{kT}\right)^{\bar{\nu}} K$$

where $\Delta_\mathrm{r} G_\mathrm{m}^\circ = N_\mathrm{A} \sum \mu_{i,\mathrm{id}}$ is the reaction molar Gibbs energy (for p = standard pressure) and K is the equilibrium constant (for the standard state ideal gas at pressure p).

Reaction step

- Random change of the extent of the reaction: with probalility 1/2 "→" ($\zeta^\mathrm{tr} = \zeta + 1$) with probalility 1/2 "←" ($\zeta^\mathrm{tr} = \zeta - 1$)
- Random selection of the corresponding number of reactant and product molecules
- Replacement of reactants → products (for $\Delta\zeta = \zeta^\mathrm{tr} - \zeta > 0$) or products → reactants (for $\Delta\zeta < 0$)
- Calculate the energy change ΔU
- New configuration accepted with probability p_acc

Note: Some degrees of freedom are simulated, some not...

Nonspherical molecules:

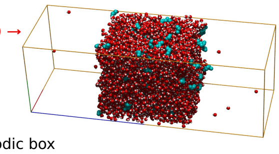
$$\exp\left[\frac{-\mu_{i,\mathrm{id}}}{kT}\right] = \frac{q_i k_\mathrm{B} T}{q_i^\mathrm{model} p^\mathrm{st}}, \quad q_i^\mathrm{model} = \int \exp(-\beta U_\mathrm{int}) \mathrm{d}(\text{intern.deg.of freedom})$$

Eg., general hard molecule: $q_i^\mathrm{model} = 8\pi^2 \Rightarrow K'$ must be divided by product $\prod_{i=1}^{k} (q_i^\mathrm{model})^{\nu_i}$

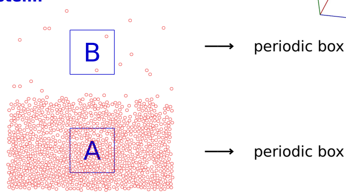
- Again, gradual insertion may be needed
- Final result = equilibrium composition

Gibbs ensemble

Determine vapor–liquid (fluid–fluid) phase equilibrium:
1) MD: slab geometry, bad for low T (water + BuOH, 373 K) →
2) MC, MD: μ in the liquid, μ gas from the virial EoS
3) Gibbs ensemble [A. Panagiotopoulos (1987)]



One-component system:



- T = const, $V = V_A + V_B$ = const, $N = N_A + N_B$ = const
  ⇒ to be satisfied: $p_A = p_B$ and $\mu_A = \mu_B$
- Gibbs phase law: 1 degree of freedom ⇒ pressure is determined

Gibbs ensemble: one-component system

$$Q_\mathrm{NVT} = \sum_{N_A=0}^{N} \int_0^V \frac{\mathrm{d}V_A V_A^{N_A}}{N_A!} \int \mathrm{d}\vec{\xi}_A^N \mathrm{e}^{-\beta U_A(N_A)} \frac{V_B^{N_B}}{N_B!} \int \mathrm{d}\vec{\xi}_B^N \mathrm{e}^{-\beta U_B(N_B)}$$

- Volume change $V_A^\mathrm{tr} = V_A + \Delta V$ a $V_B^\mathrm{tr} = V_B - \Delta V$, acceptance probability:

$$p_\mathrm{acc} = \min\left\{1, \exp\left[-\beta\Delta U_A - \beta\Delta U_B + N_A \ln\frac{V_A + \Delta V}{V_A} + N_B \ln\frac{V_B - \Delta V}{V_B}\right]\right\}$$

- Particle transfer from box B to box A, acceptance probability:

$$p_\mathrm{acc} = \min\left\{1, \exp\left[-\beta\Delta U_A - \beta\Delta U_B - \ln\frac{(N_A + 1)V_B}{N_B V_A}\right]\right\}$$

- Particle transfer from box A to box B, acceptance probability:

$$p_\mathrm{acc} = \min\left\{1, \exp\left[-\beta\Delta U_B - \beta\Delta U_A - \ln\frac{(N_B + 1)V_A}{N_A V_B}\right]\right\}$$

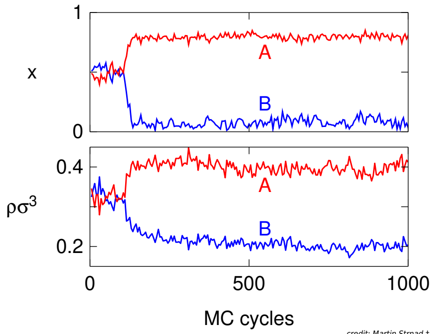
- Standard MC moves – translations, rotations.

Usually 1 volume change + 1–several article transfers per N single-particle moves.

Gibbs ensemble: mixture

Gibbs phase law for a binary mixture: 2 degrees of freedom
T = const, p = const, equilibrium compositions are determined

- Volume changes in both boxes separately (see NPT)
- Particle transfer
- Useful: particle exchange between boxes – higher probability



credit: Martin Strnad †