Compressibility and fluctuations I

Identical particles in the (classical) grand canonical ensemble (μVT), $G = \mu N$ (μ is per molecule):

$$\Omega = F - \mu N = F - G = -pV = -k_\mathrm{B}T \ln Z_{\mu VT}, \quad \text{where } Z_{\mu VT} = \sum_{N=0}^{\infty} \frac{\mathrm{e}^{\beta\mu N}}{N! h^{3N}} \int \mathrm{e}^{-\beta E} \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{p}_N$$

Let's temporarily distinguish $\langle N \rangle$ and the summation index N

$$\langle N \rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = k_\mathrm{B}T \left(\frac{\partial \ln Z_{\mu VT}}{\partial \mu}\right)_{T,V} = \frac{\sum_0^\infty N \frac{\mathrm{e}^{\beta\mu N}}{N! h^{3N}} \int \mathrm{e}^{-\beta E} \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{p}_N}{\sum_0^\infty \frac{\mathrm{e}^{\beta\mu N}}{N! h^{3N}} \int \mathrm{e}^{-\beta E} \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{p}_N} = \frac{\sum_{N=0}^\infty N \frac{\mathrm{e}^{\beta\mu N}}{N! \Lambda^{3N}} Q_N}{\sum_{N=0}^\infty \frac{\mathrm{e}^{\beta\mu N}}{N! \Lambda^{3N}} Q_N},$$

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

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

$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N$
$\mathrm{d}\Omega = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu$

Compressibility and fluctuations II

The state in the **thermodynamic limit** is defined by intensive variables:

$$\boldsymbol{\rho} = \frac{\langle N \rangle_{\mu VT, V\to\infty}}{V} = \frac{N}{\langle V \rangle_{NVT, N\to\infty}}$$

$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N$
$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}N$
$\mathrm{d}\Omega = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu$

For constant $[T, N]$ it holds $\mathrm{d}G = V\mathrm{d}p$, but also $\mathrm{d}G = \mathrm{d}(\mu N) = N\mathrm{d}\mu$.
If the state change at $[T]$ is caused by changing $\boldsymbol{\rho}$:

$$V \left(\frac{\partial p}{\partial \boldsymbol{\rho}}\right)_T = N \left(\frac{\partial \mu}{\partial \boldsymbol{\rho}}\right)_T$$

Can be derived also with $/\partial\boldsymbol{\rho}$ replaced by $/\partial N$ or $/\partial V$.

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

The state at $[T]$ can be equivalently changed using either N or V:

$$V \left(\frac{\partial p}{\partial \boldsymbol{\rho}}\right)_T = V \left(\frac{\partial p}{\partial (N/V)}\right)_{T,N} = \frac{V}{N} \left(\frac{\partial p}{\partial (1/V)}\right)_{T,N} = \frac{V}{N} \left(\frac{\partial p}{\partial V}\right)_{T,N} \Big/ \frac{\mathrm{d}(1/V)}{\mathrm{d}V} = \frac{V^2}{N\kappa_T}$$

$$N \left(\frac{\partial \mu}{\partial \boldsymbol{\rho}}\right)_T = N \left(\frac{\partial \mu}{\partial (N/V)}\right)_{T,V} = VN \left(\frac{\partial \mu}{\partial N}\right)_{T,V} = \frac{NV}{\beta \operatorname{Var} N}$$

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

Together: $\frac{\operatorname{Var} N}{\langle N \rangle} = \boldsymbol{\rho} k_\mathrm{B} T \kappa_T$ or equivalently: $\frac{\operatorname{Var} N}{\langle N \rangle} = \frac{\kappa_T}{\kappa_T^{\text{id. plyn}}}$

Compressibility and fluctuations III

$$\frac{\operatorname{Var} N}{\langle N \rangle} = \frac{\kappa_T}{\kappa_T^{\text{id. gas}}}$$

- larger compressibility ⇒ larger fluctuations
- $\operatorname{Var} N > 0 \Rightarrow \kappa_T > 0$ ($\kappa_T < 0$ for a mechanically unstable system)
- $\operatorname{Var} \boldsymbol{\rho} = \frac{\boldsymbol{\rho}^2 \kappa_T}{N \kappa_T^{\text{id. gas}}} \overset{N\to\infty}{=} 0$ (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 I

$$\boldsymbol{\rho}^2 g(r) = \frac{\sum_{N=2}^\infty N(N-1) \frac{\mathrm{e}^{\beta\mu N}}{N! \Lambda^{3N}} \int \exp(-\beta U) \mathrm{d}\vec{r}_3 \ldots \mathrm{d}\vec{r}_N}{\sum_{N=0}^\infty \frac{\mathrm{e}^{\beta\mu N}}{N! \Lambda^{3N}} \int \exp(-\beta U) \mathrm{d}\vec{r}_1 \ldots \mathrm{d}\vec{r}_N}, \qquad r = |\vec{r}_1 - \vec{r}_2|$$

⇒ **Compressibility equation** $1 + \boldsymbol{\rho} \int [g(r) - 1] \mathrm{d}\vec{r} = \frac{\operatorname{Var} N}{\langle N \rangle} = \boldsymbol{\rho} k_\mathrm{B} T \kappa_T$

spherical symmetry: $\int \mathrm{d}\vec{r} = \int_0^\infty 4\pi r^2 \mathrm{d}r$

Proof: $\boldsymbol{\rho} = \langle N \rangle / V$

$$\boldsymbol{\rho} \int g(\vec{r}) \mathrm{d}\vec{r} = \frac{\boldsymbol{\rho}}{V} \int g(\vec{r}_{12}) \mathrm{d}\vec{r}_{12} \mathrm{d}\vec{r}_1 \overset{J=1}{=} \frac{\boldsymbol{\rho}}{V} \int g(\vec{r}_{12}) \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2 = \frac{\boldsymbol{\rho}}{V} \frac{\langle N(N-1) \rangle}{\boldsymbol{\rho}^2} = \frac{\langle N(N-1) \rangle}{\langle N \rangle}$$

$$\boldsymbol{\rho} \int 1 \mathrm{d}\vec{r}_{12} = \frac{\langle N \rangle}{V} V = \langle N \rangle$$

all three terms together:

$$1 + \boldsymbol{\rho} \int [g(r) - 1] \mathrm{d}\vec{r} = \frac{\langle N \rangle + \langle N(N-1) \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{\operatorname{Var} N}{\langle N \rangle}$$

RDF in the μVT ensemble and compressibility I

- 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 it holds $\mathrm{e}^{\beta\mu N}/\Lambda^3 = p/k_\mathrm{B}T = \langle N \rangle / V = \boldsymbol{\rho}$

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

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

Typical error $\propto 1/N \to 0$ for $N \to \infty$ *

Corrections:

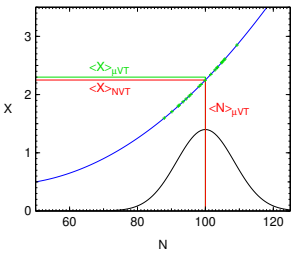
$$\langle X \rangle_{\mu VT} - \langle X \rangle_{NVT} \approx \frac{1}{2} \left\langle (N - \langle N \rangle_{\mu VT})^2 \right\rangle_{\mu VT} \left(\frac{\partial^2 \langle X \rangle_{\mu VT}}{\partial N^2}\right)_{T,V} \quad (N = \langle N \rangle_{\mu VT})$$

$$= \frac{k_\mathrm{B}T}{2N} \left(\frac{\partial \boldsymbol{\rho}}{\partial p}\right)_T \boldsymbol{\rho}^2 \left(\frac{\partial^2 \langle X \rangle}{\partial \boldsymbol{\rho}^2}\right)_T$$

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

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

The corrections become important near the critical point



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

MC in the microcanonical ensemble

MC move under constraint $E = \text{const}$ = problem

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

Approximate solution – Creutz

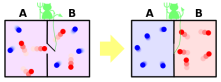
$$E = E_\text{max} \quad \to \quad E \le E_\text{max}$$

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

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

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

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

in all cases $\langle \text{bag} \rangle = k_\mathrm{B}T$ (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: $\vec{r}_i = V^{1/3} \vec{\xi}_i$

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

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

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

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

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

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

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

- Usually N one-particle moves (translations:rotations = 1:1) per one volume-change move
- Acceptance ratio of volume changes: 0.3 or a bit more (0.4)
- 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

$\vec{r}_i = V^{1/3} \vec{\xi}_i$

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

$\mathrm{d}\vec{r}^N$ depends on N ⇒ dimensionless coordinates $\vec{r}_i = V^{1/3} \vec{\xi}_i$

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

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

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

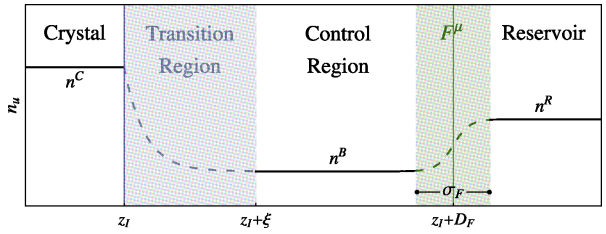
$$p_\text{remove particle} = \min\left\{1, \frac{N\Lambda^3}{\mathrm{e}^{\beta\mu} V} \exp\{-\beta[U_{N-1}(\vec{r}^{N-1,\text{zkus}}) - U_N(\vec{r}^N)]\}\right\}$$

Problem: insert a large molecule
Solution: gradually

$\mathrm{e}^{\beta\mu} = \Lambda^3 \mathrm{e}^{\beta\mu_\text{res}} \langle N \rangle / V$

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: $\Delta_r G_m = \sum_{i=1}^{k} \nu_i \mu_i = 0$

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

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

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

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

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

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

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

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

where $\Delta_r G^\circ_m = N_A\sum\mu_{i,\mathrm{id}}$ 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:

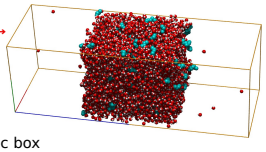
$$\exp\left[\frac{-\mu_{i,\mathrm{id}}}{kT}\right] = \frac{q_i k_B T}{q_i^{\mathrm{model}} p^{\mathrm{st}}},\quad q_i^{\mathrm{model}} = \int \exp(-\beta U_{\mathrm{int}})\mathrm{d}(\text{intern.deg.of freedom})$$

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

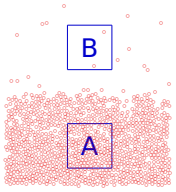
- Again, gradual insertion may be needed
- Final result = equilibrium composition

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:



⟶ periodic box

⟶ periodic box

- 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:

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

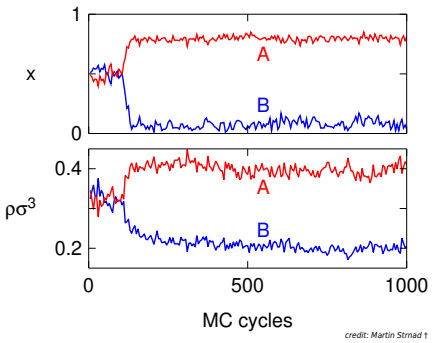
- Standard MC moves – translations, rotations.

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

Gibbs ensemble: binary 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 †