Compressibility and fluctuations

Grandcanonical partition function in semiclassical approximation:

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

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

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

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

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

Compressibility and fluctuations

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

Grandcanonical potential: $\Omega = F - N\mu = -pV = -\beta\ln Z_{\mu VT}$

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

Differential: $\mathrm{d}\Omega = -p\mathrm{d}V - V\mathrm{d}p = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu \;\Rightarrow\; N\mathrm{d}\mu = V\mathrm{d}p\;\;[T,N,V]$

Another derivation: $\mathrm{d}G = N\mathrm{d}\mu = V\mathrm{d}p\;\;[T,N]$

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:

$$\frac{\mathrm{Var}\,N}{\langle N\rangle} = \rho k_\mathrm{B} T\kappa_T$$

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

$$\frac{\operatorname{Var} N}{\langle N\rangle} = \rho k_\mathrm{B} T \kappa_T$$

- larger compressibility ⇒ larger fluctuations
- $\operatorname{Var} N > 0 \Rightarrow \kappa_T > 0$ ($\kappa_T < 0$ for a mechanically unstable system)
- $\operatorname{Var}\rho = \dfrac{\rho^3 k_\mathrm{B} T \kappa_T}{N} \overset{N\to\infty}{=} 0$ (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

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

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

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

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

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:

$N = \langle N \rangle_{\mu VT}$

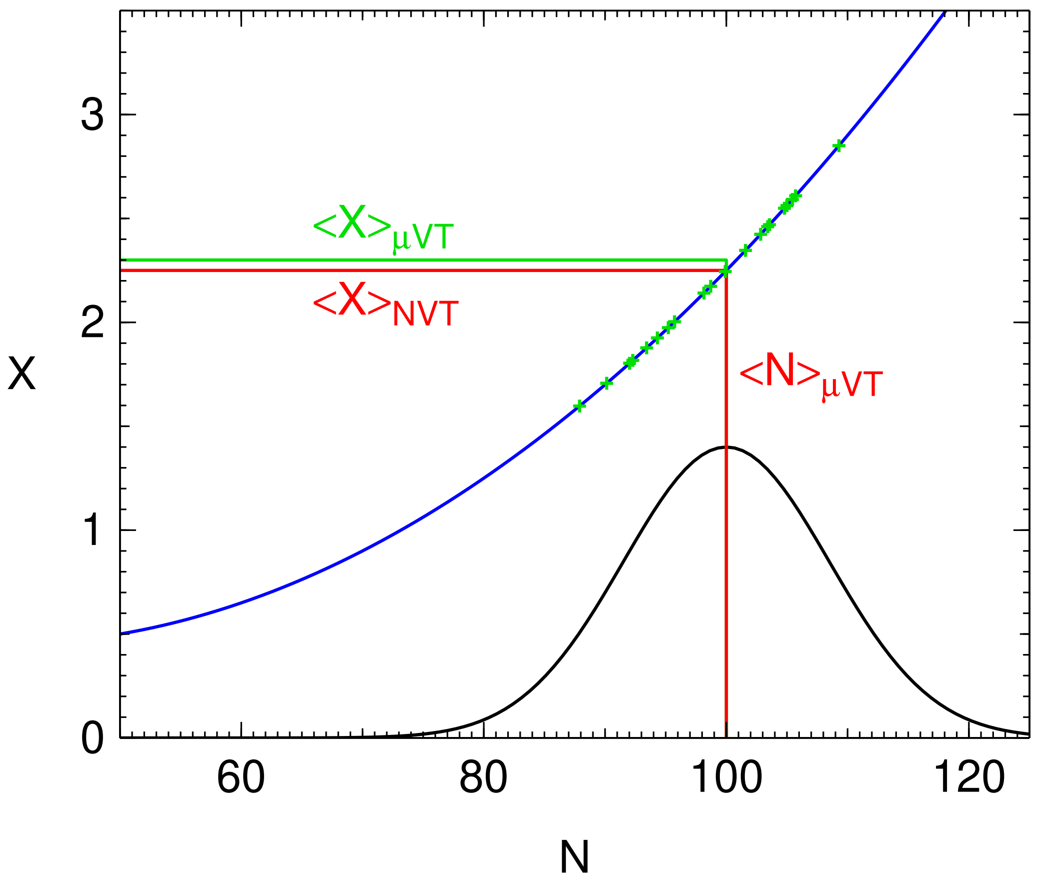
$$\langle X \rangle_{\mu VT} - \langle X \rangle_{NVT} \approx \frac{1}{2} \left\langle (N - \langle N \rangle_{\mu VT})^2 \right\rangle_{\mu VT} \left(\frac{\partial^2 \langle X \rangle_{\mu VT}}{\partial N^2} \right)_{V,T}$$

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

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 $E = \mathrm{const}$ = problem

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

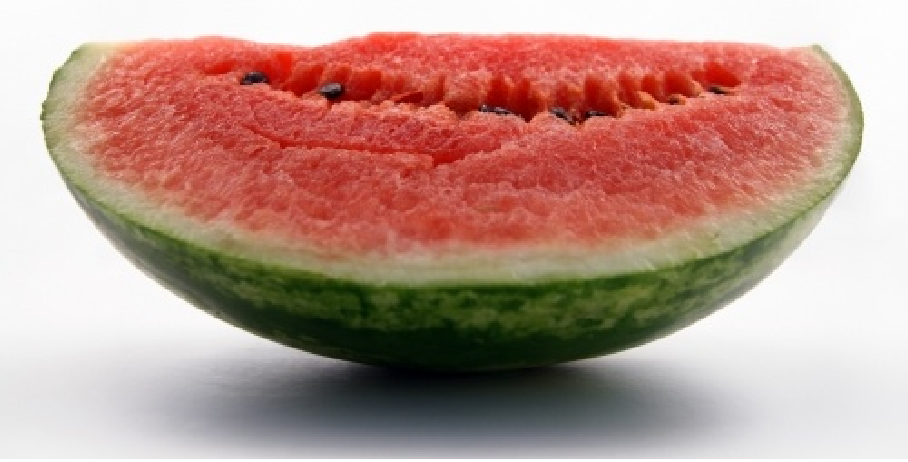
Approximate solution – Creutz

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

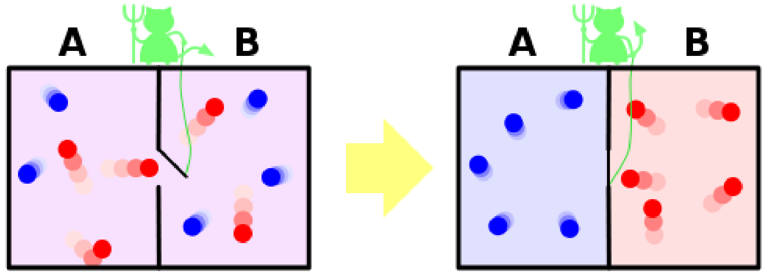
(do not buy a melon in a many-dimensional space)

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

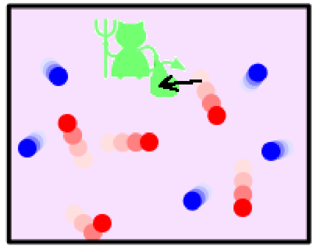
E_{bag} has the Boltzmann distribution ⇒ temperature



Maxwell's demon



Creutz's demon



Credit: Wikipedia (modified)

Creutz – Metropolis comparison

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

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

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

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

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

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

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

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

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

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

- 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

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

- MC step: change the number of particles by ±1

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

$d\vec{r}^N$ 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

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

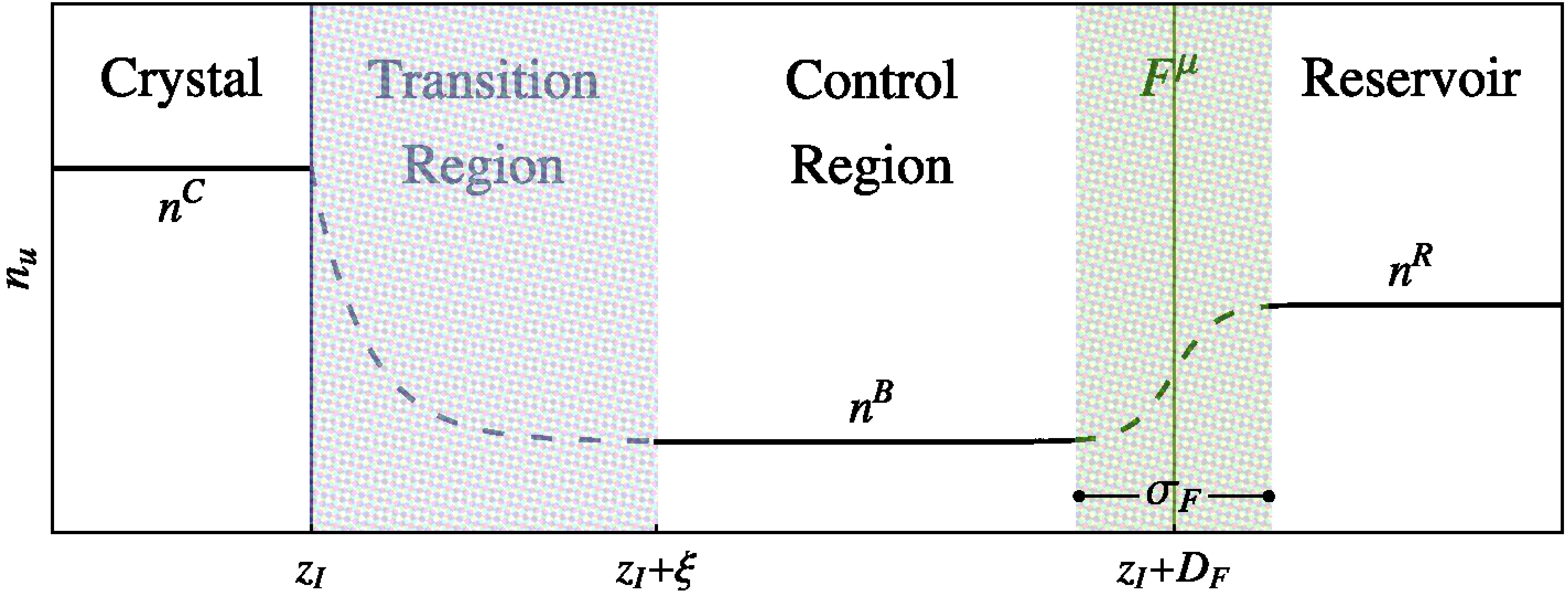
$$p_{\text{remove particle}} = \min\left\{1, \frac{N\Lambda^3}{e^{\beta\mu}V}\exp\{-\beta[U_{N-1}(\vec{r}^{N-1,\text{zkus}}) - U_N(\vec{r}^N)]\}\right\}$$

Problem: insert a large molecule
Solution: gradually

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

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

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

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

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

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

Reaction ensemble in MC

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

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

where

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

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

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

where $\Delta_{\rm r}G^\circ_{\rm m} = N_{\rm A} \sum \mu_{i,\rm id}$ 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 "→" ($\zeta^{\rm tr} = \zeta + 1$) with probalility 1/2 "←" ($\zeta^{\rm tr} = \zeta - 1$)
- Random selection of the corresponding number of reactant and product molecules
- Replacement of reactants → products (for $\Delta\zeta = \zeta^{\rm tr} - \zeta > 0$) or products → reactants (for $\Delta\zeta < 0$)
- Calculate the energy change ΔU
- New configuration accepted with probability $p_{\rm acc}$

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

Nonspherical molecules:

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

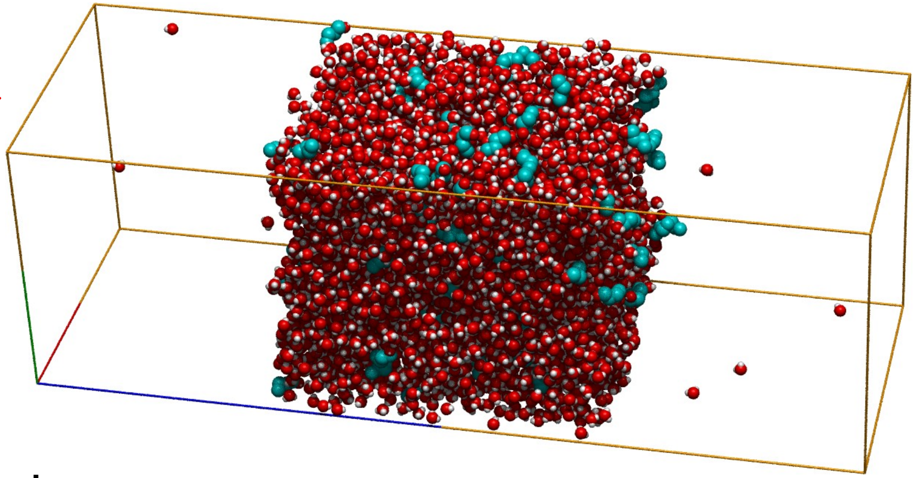
Eg., general hard molecule: $q_i^{\rm model} = 8\pi^2 \Rightarrow K'$ must be divided by product $\prod_{i=1}^{k} (q_i^{\rm model})^{\nu_i}$

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

Gibbs ensemble

Determine vapor–liquid (fluid–fluid) phase equilibrium:

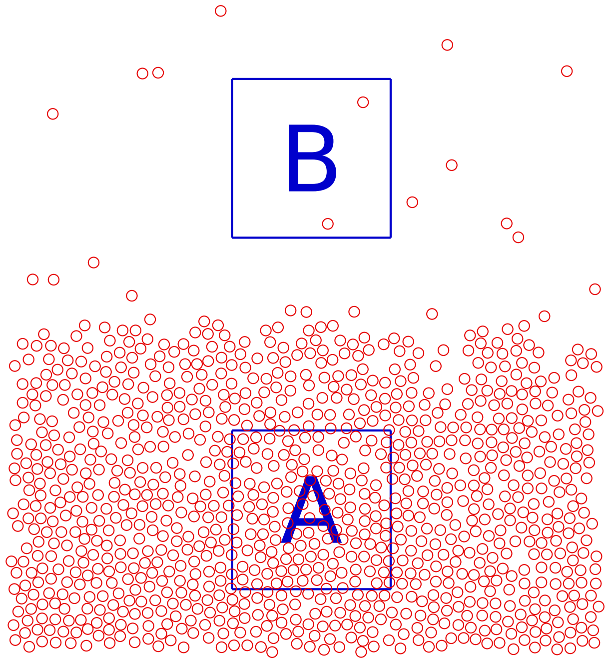
1) MD: slab geometry, bad for low T (water + BuOH, 373 K) →



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

- $T = \text{const}$, $V = V_A + V_B = \text{const}$, $N = N_A + N_B = \text{const}$
  ⇒ 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

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

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

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

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

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

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

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

- Standard MC moves – translations, rotations.

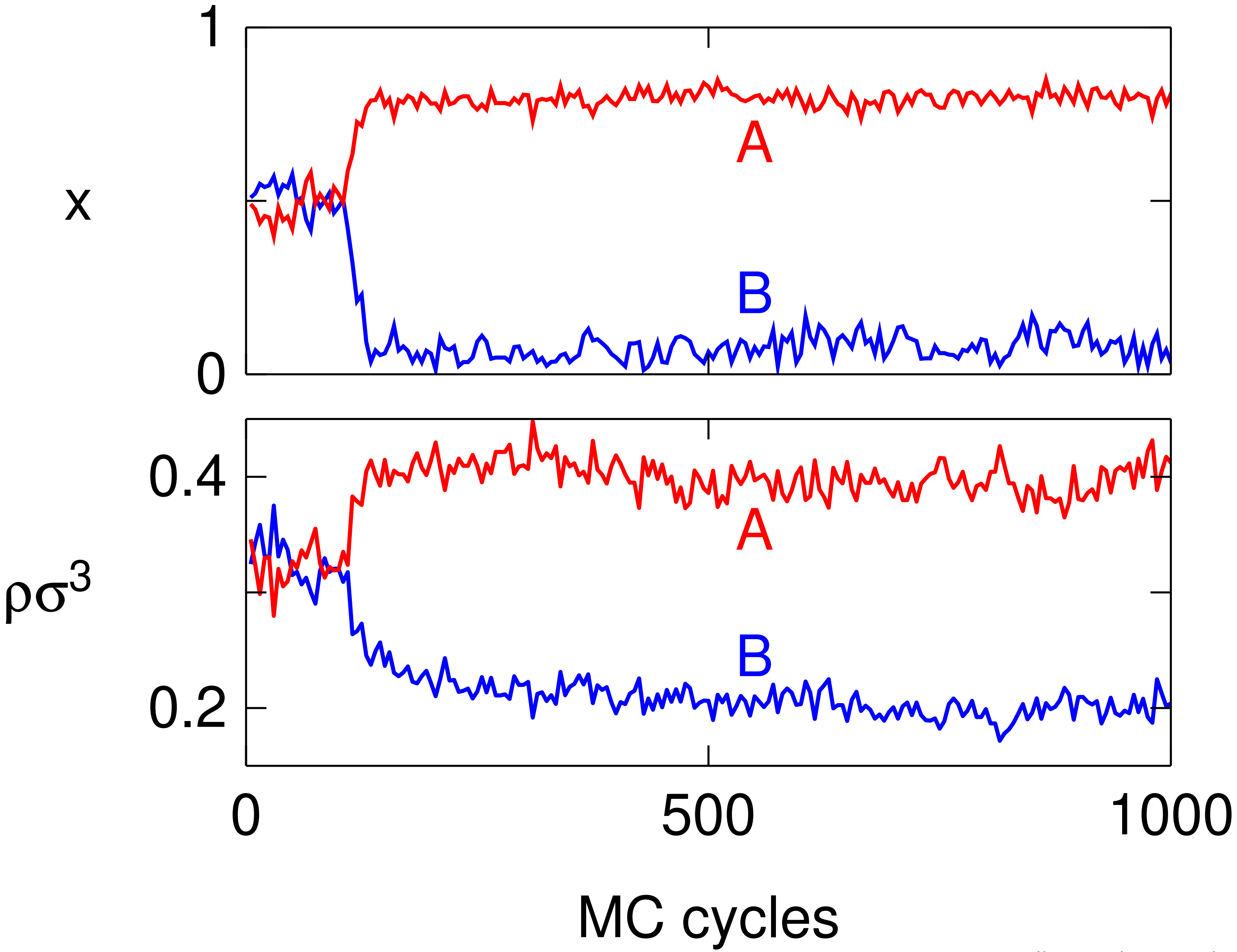
Usually 1 volume change + 1–several article transfers per N single-particle moves.

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 †