

Grandcanonical partition function in semiclassical approximation:

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

System of N identical particles in the grandcanonical ensemble (μVT), $\mu =$ parameter

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

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

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

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

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

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

Another derivation: $dG = Nd\mu = Vdp \quad [T, N]$

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:

$$\frac{\text{Var} N}{\langle N \rangle} = \rho k_B T \kappa_T$$

isothermal compressibility:

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

bulk modulus:

$$B_T = 1/\kappa_T$$

$$\frac{\text{Var } N}{\langle N \rangle} = \rho k_B T \kappa_T$$

- larger compressibility \Rightarrow larger fluctuations
- $\text{Var } N > 0 \Rightarrow \kappa_T > 0$ ($\kappa_T < 0$ for a mechanically unstable system)
- $\text{Var } \rho = \frac{\rho^3 k_B T \kappa_T}{N} \stackrel{N \rightarrow \infty}{\equiv} 0$ (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

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

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

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

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

Exercise 2. Calculate κ_T from the compressibility equation with the canonical RDF ($N = \text{constant}$)

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

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

Corrections:

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

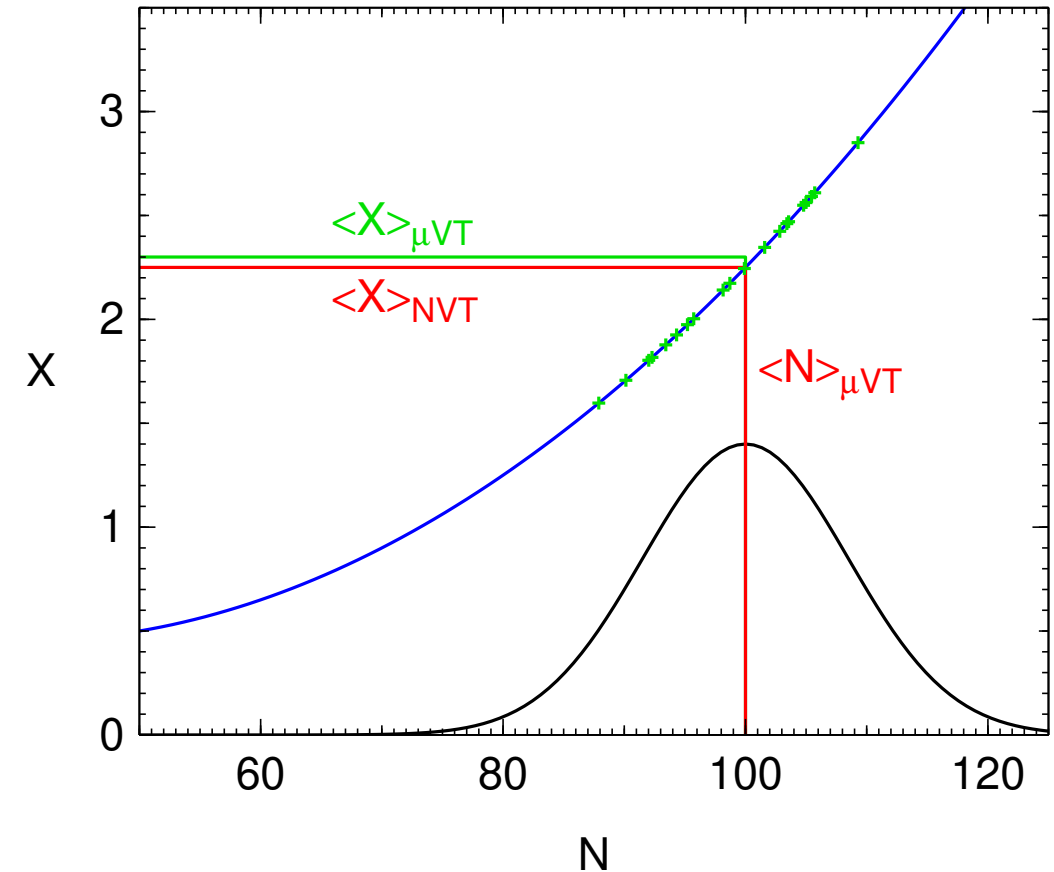
$N = \langle N \rangle_{\mu VT}$

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

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 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).

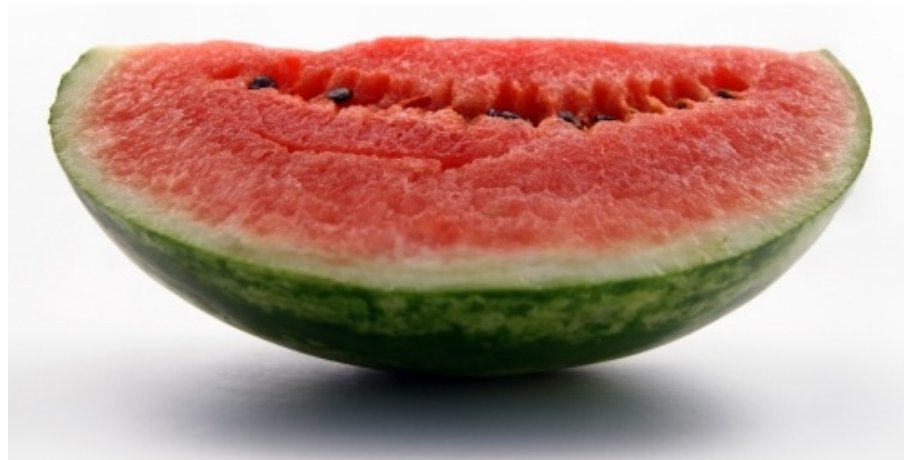
Approximate solution – Creutz

$$E = E_{\text{max}} \quad \rightarrow \quad E \leq E_{\text{max}}$$

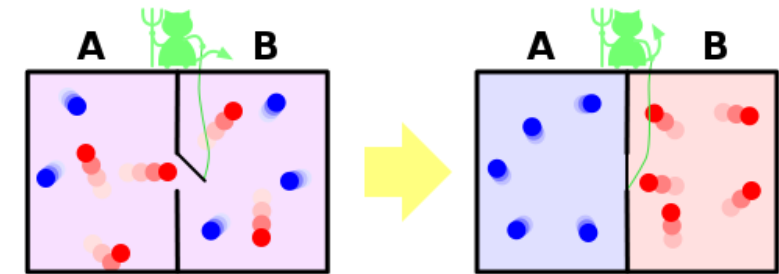
(do not buy a melon in a many-dimensional space)

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

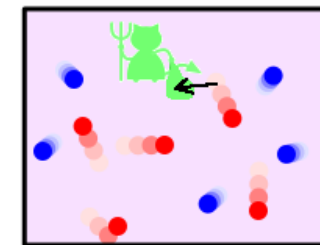
E_{bag} has the Boltzmann distribution \Rightarrow temperature



Maxwell's demon



Creutz's demon



Credit: Wikipedia (modified)

Creutz – Metropolis comparison

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

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

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

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

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

$$\begin{aligned} \langle X \rangle &= \frac{1}{Q_{\text{NPT}}} \int_0^\infty \left(\int_{V^N} X(\vec{r}^N, V) \frac{N}{V} \exp\{-\beta[pV + U(\vec{r}^N)]\} d\vec{r}^N \right) dV \\ &= \frac{1}{Q_{\text{NPT}}} \int_0^\infty \int_{1^{3N}} X(V^{1/3} \vec{\xi}^N, V) \frac{N}{V} V^N \exp\{-\beta[pV + U(V^{1/3} \vec{\xi}^N)]\} d\vec{\xi}^N dV \end{aligned}$$

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

$N/V, -1$: exact ideal gas
 $\beta p, \text{const}$: $\mathcal{O}(1/N)$ 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 ration of volume changes ~ 0.3
- General problem: global change of configuration \Rightarrow slow convergence \Rightarrow not good for too large systems

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

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

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

$d\vec{r}^N$ depends on $N \Rightarrow$ 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

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

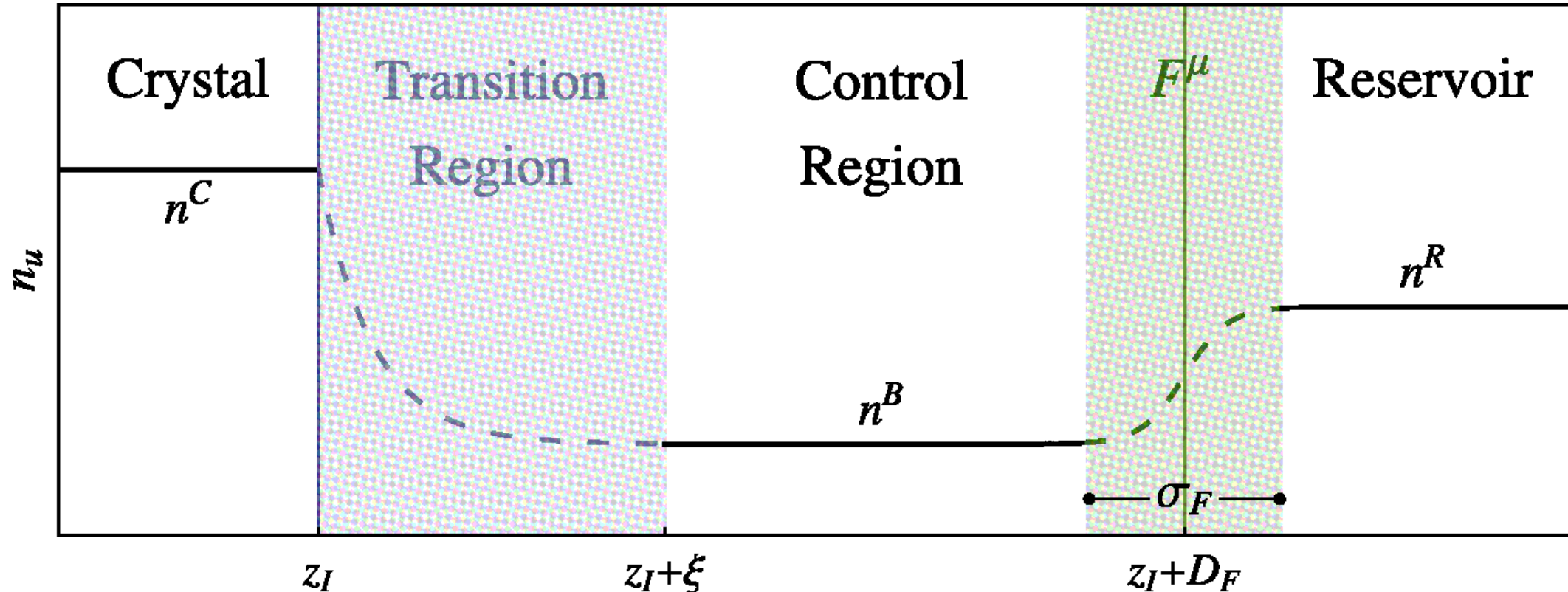
$$p_{\text{remove particle}} = \min \left\{ 1, \frac{N \Lambda^3}{e^{\beta\mu} V} \exp \left\{ -\beta [U_{N-1}(\vec{r}^{N-1, \text{zkus}}) - U_N(\vec{r}^N)] \right\} \right\}$$

Problem: insert a large molecule

Solution: gradually

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

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



● We can easily calculate a chemical equilibrium in an ideal gas phase.

But what if the mixture is not ideal? 1) Calculate $\mu_i, \gamma_i \dots$ 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):

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

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

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

Reaction “move” $\zeta^{\text{tr}} = \zeta + \Delta\zeta$ accepted with probability

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

where

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

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

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

where $\Delta_r G_m^\circ = N_A \sum \mu_{i,\text{id}}$ 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).

- Random change of the extent of the reaction: with probability 1/2 “→” ($\zeta^{\text{tr}} = \zeta + 1$) with probability 1/2 “←” ($\zeta^{\text{tr}} = \zeta - 1$)
- Random selection of the corresponding number of reactant and product molecules
- Replacement of reactants → products (for $\Delta\zeta = \zeta^{\text{tr}} - \zeta > 0$) 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:

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

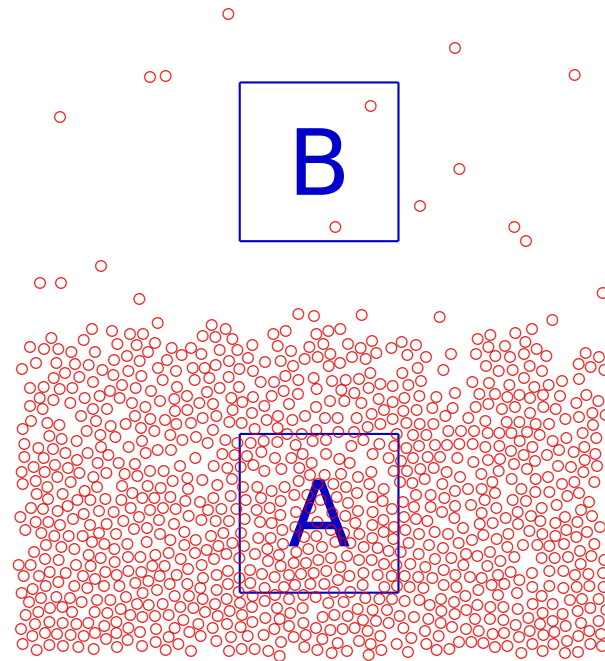
Eg., general hard molecule: $q_i^{\text{model}} = 8\pi^2 \Rightarrow K'$ must be divided by product $\prod_{i=1}^k (q_i^{\text{model}})^{\nu_i}$

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

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

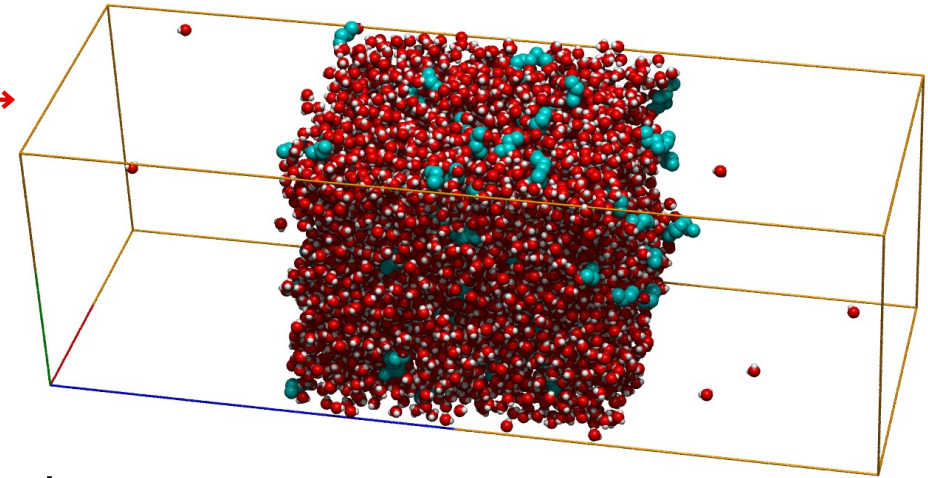
- 1) MD: slab geometry, bad for low T (water + BuOH, 373 K) →
- 2) MC, MD: μ in the liquid, μ gas from the virial EoS
- 3) Gibbs ensemble [A. Panagiotopoulos (1987)]

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

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

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

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

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

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

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

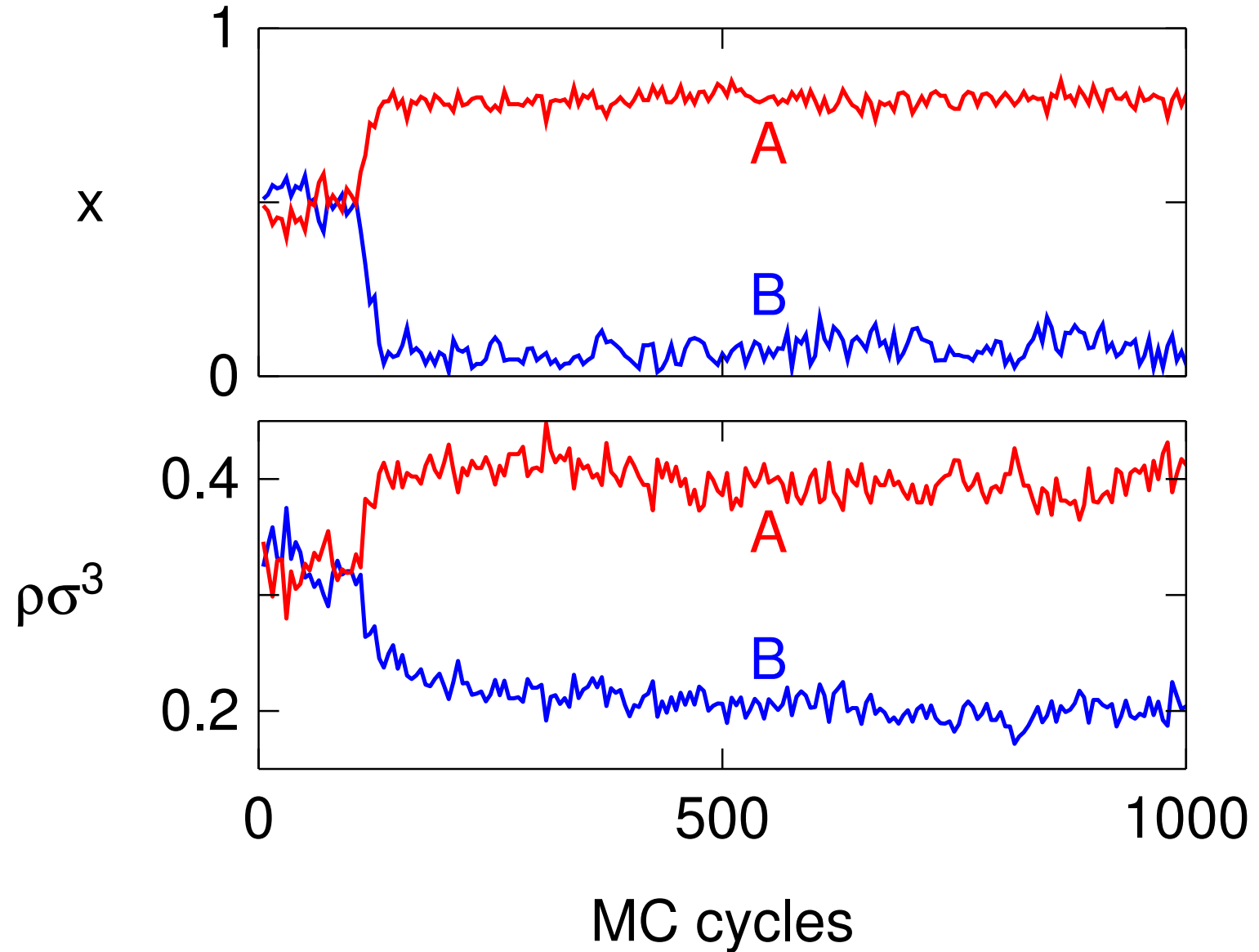
$$p_{\text{acc}} = \min \left\{ 1, \exp \left[-\beta \Delta U_B - \beta \Delta U_A - \ln \frac{(N_B + 1)V_A}{N_A V_B} \right] \right\}$$

- Standard MC moves – translations, rotations.

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

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

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



Exercise – Madelung constant of NaCl

+ 17/17
s10/4

For the electrostatic energy of a crystal it holds (per 1 molecule of NaCl)

$$E_{\text{el}} = \frac{Ma^2}{4\pi\epsilon_0 a}$$

where a = lattice constant and M = Madelung constant

- Simulate a NaCl crystal while decreasing temperature to zero.

Use data:

```
T=0 tau.T=0.2
```

```
cutoff=8 LJcutoff=cutoff
```

```
tau.P=0.2 bulkmodulus=1e11 ;
```

```
! restart after cooling
```

```
el.epsk=0.1 el.epsr=0.1 el.grid=1024 ! higher precision
```

```
init="start" no=1;
```

- Determine the box size and calculate a
- Determine the electrostatic energy and express it per 1 NaCl
- Calculate the Madelung constant