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: $\mu \to N$

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

Corrections:

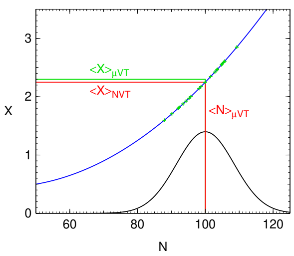
$$\langle X\rangle_{\mu VT} - \langle X\rangle_{NVT} \approx \frac{1}{2}\left\langle (N - \langle N\rangle_{\mu VT})^2\right\rangle_{\mu VT} \left(\frac{\partial^2 \langle X\rangle_{\mu VT}}{\partial N^2}\right)_{V,T}, \quad N = \langle N\rangle_{\mu VT}$$

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

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

Derivation: Taylor expansion of $X(N)$ 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 $E_{pot} + E_{kin} = \text{const}$: can be integrated over momenta (not so trivial, though).

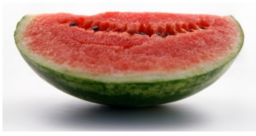
Approximate solution – Creutz

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

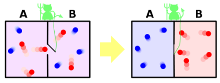
(do not buy a melon in a many-dimensional space)

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

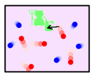
E_{bag} has the Boltzmann distribution ⇒ temperature



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

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

Other ensembles

- *NPT* (isothermal-isobaric) ensemble = standard Metropolis + volume change with a Metropolis-like acceptance formula containing barostat pressure
- μVT (grand canonical) ensemble = standard Metropolis + insert (to a random place) or remove a molecule with a Metropolis-like acceptance formula containing μ
- Reaction ensemble = standard Metropolis + make reaction; e.g. for reaction

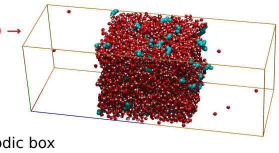
$$A + B \to AB$$

(i) change A into AB and remove B;
(ii) change AB into A and insert B into a random place.
Input: equilibrium constant in the gas phase
Output: equilibrium composition in a non-ideal system (dense gas, liquid)

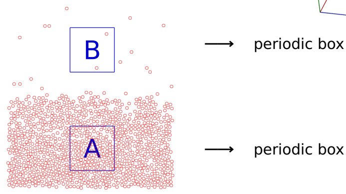
- Vapor-liquid equilibrium (Gibbs ensemble): two boxes, each with different phase, standard Metropolis + transfer of molecules between boxes,
one phase: total volume constant, change of relative volume,
more phases: *NPT* in each box

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:



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

Gibbs ensemble: mixture

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