Isothermal-Isobaric MC (NPT ensemble)

Most lab experiments are carried out at const. pressure and temperature. The NPT ensemble is often desirable for computer simulations to obtain equation-of-state data or (qualitative!) information on phase transitions.

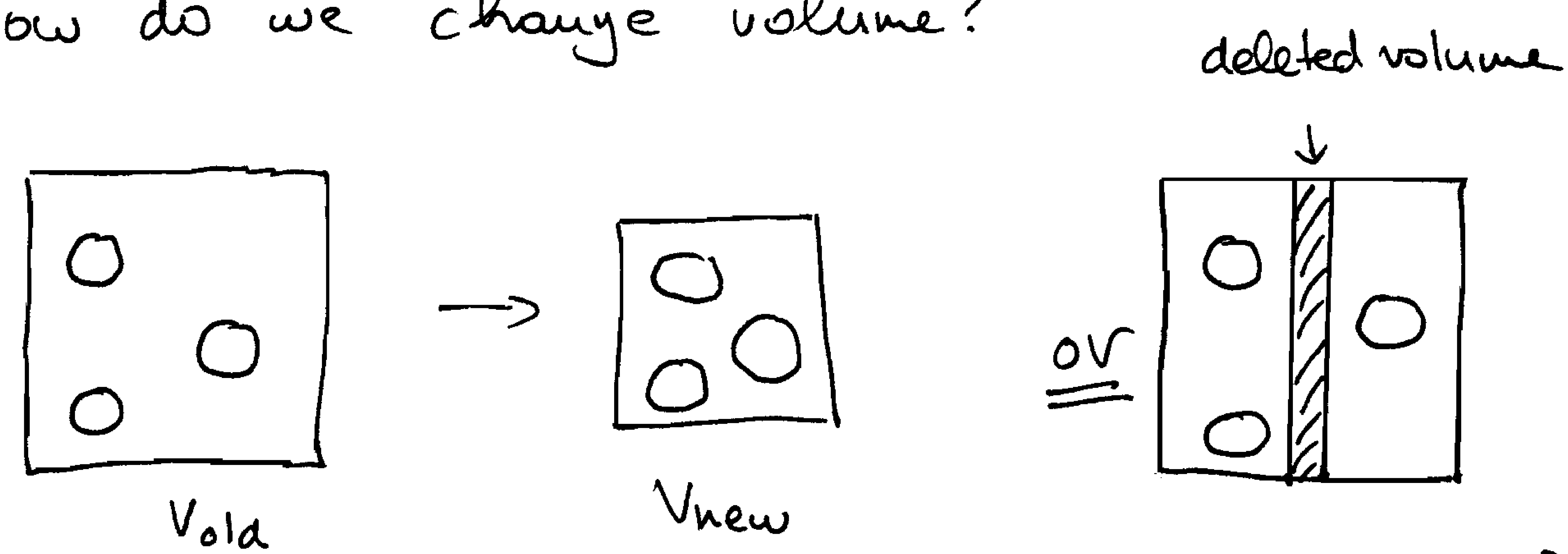
Probabilities of microstates in NPT ensemble (see Stat. Mech. handout): $\mathcal{P}_v \propto \exp(-\beta U_v - \beta P V_v)$

Fluctuations in volume <u>must</u> be sampled!

At thermodynamic limit, these are

$$\langle(\delta V)^2\rangle = -kT \underbrace{\left(\frac{\partial V}{\partial P}\right)_{T,N}}_{\text{isothermal compressibility}}$$

How do we change volume?



(A) {scale positions} good for continuous potentials

(B) (no scaling) good for lattice models

For coordinate scaling, must have:

$$\mathcal{P}_{old} \propto V_{old}^N \exp(-\beta U_{old} - \beta P V_{old})$$

↑ "entropic" term to take into account density of states in old and rescaled volumes

$$\mathcal{P}_{new} \propto V_{new}^N \exp(-\beta U_{old} - \beta P V_{new})$$

$$\frac{\mathcal{P}_{new}}{\mathcal{P}_{old}} = \left(\frac{V+\Delta V}{V}\right)^N \exp(-\beta \Delta U - \beta P \Delta V) \quad (A) \qquad \underbrace{P_{acc} = \min\left\{1, \frac{\mathcal{P}_{new}}{\mathcal{P}_{old}}\right\}}_{\text{Metropolis}}$$

For volume creation/annihalation, the particles do not move, so no V^N term is present:

$$\frac{\mathcal{P}_{new}}{\mathcal{P}_{old}} = \exp(-\beta \Delta U - \beta P \Delta V) \quad (B) \qquad P_{acc} = \min\left\{1, \frac{\mathcal{P}_{new}}{\mathcal{P}_{old}}\right\}$$

To check on these (and any other) acceptance criteria, a good 1st test is to determine the PVT relationship (equation-of-state) of a system of non-interacting particles undergoing a "virtual simulation": at equilibrium, $P_{acc}^+ = P_{acc}^-$, $\Delta U = \varnothing$ (no interactions)

case (A) for <u>any</u> ΔV, $P_{acc}^+ = P_{acc}^- \Rightarrow \left(\frac{V+\Delta V}{V}\right)^N e^{-\beta P \Delta V} = 1$

$$\Rightarrow \underbrace{\left(1 + \frac{\Delta V}{V}\right)^N = e^{\beta P \Delta V} \Rightarrow}_{\text{Taylor expand, } \Delta V/V \ll 1} \cancel{1} + \frac{N \cancel{\Delta V}}{V} = \cancel{1} + \beta P \cancel{\Delta V} \Rightarrow \boxed{\beta P = \rho}$$

✓ checks – I.6, EOS

Case (B) $P_{acc}^{+} = P_{acc}^{-} \Rightarrow e^{-\beta P \Delta V} = P_{acc}^{-}$

What is the probability of successfully removing ΔV volume out of V? If only one particle were present, this would be simply $\left(1-\frac{\Delta V}{V}\right)$, the probability of the particle being <u>outside</u> the removed volume. Since particles are not interacting, for N of them, $P_{acc}^{-} = \left(1-\frac{\Delta V}{V}\right)^N$

$$\therefore e^{-\beta \Delta V P} = \underbrace{\left(1-\frac{\Delta V}{V}\right)^N}_{\text{Taylor expand } \frac{\Delta V}{V} \ll 1} \Rightarrow 1 - \beta P \Delta V = -\frac{N \Delta V}{V} \Rightarrow$$

$$\boxed{\beta P = \rho} \quad \text{I.G. EOS}$$

Implementation Issues

When there is the possibility of multiple move types, we need to decide how frequently to perform each move type. The detailed balance condition (not necessary, but a good idea) requires that move types are selected at random with fixed probabilities (at least during the production period).

e.g. 1% volume changes ← expensive; cost N^2
99% displacements ← cheap; cost N or $O(1)$

Rule-of-thumb: keep CPU cost for each move type approximately constant; ratio $\frac{N \text{ displacements}}{1 \text{ volume change}}$

How do we select ΔV_{max}?

Same considerations as for dr_{max} – target acceptance of volume change moves $\sim 20-30\%$

Should volume changes be done in V, L or $\ln V$?

If large volume changes are often accepted (e.g. at low densities), it may be better to sample uniformly in $\ln V$ rather than V:

$$\left.\begin{aligned} dV &= dV_{max} \cdot (\mathrm{ranf}() - 0.5) \\ V_{new} &= V_{old} + \Delta V \end{aligned}\right\} \text{ sampling in } V$$

$$\left.\begin{aligned} dV &= dV_{max} \cdot (\mathrm{ranf}() - 0.5) \\ V_{new} &= \exp\left[\ln V_{old} + dV\right] \end{aligned}\right\} \text{ sampling in } \ln V$$

For sampling in $\ln V$, the acceptance criterion needs to be modified! $d(\ln V) = \frac{1}{V} dV \Rightarrow dV = V\, d\ln(V)$

$$P \propto V^{N+1} \exp(-\beta U - \beta P V) \implies$$

$$\frac{P_{new}}{P_{old}} = \left(\frac{V+\Delta V}{V}\right)^{N+1} \exp(-\beta \Delta U - \beta P \Delta V) \quad (c)$$

Overall Code Structure (Algorithm 10)

```
do istep = 1, nsteps
   if (ranf() < pdispl) then
      call displace (N, U, ...)
   else
      call v_change (N, U, V, ...)
   endif
   if (mod(istep, nsample) = 0) call sample ()
enddo
```

$0 < pdispl \le 1$ is the prob. of displacement