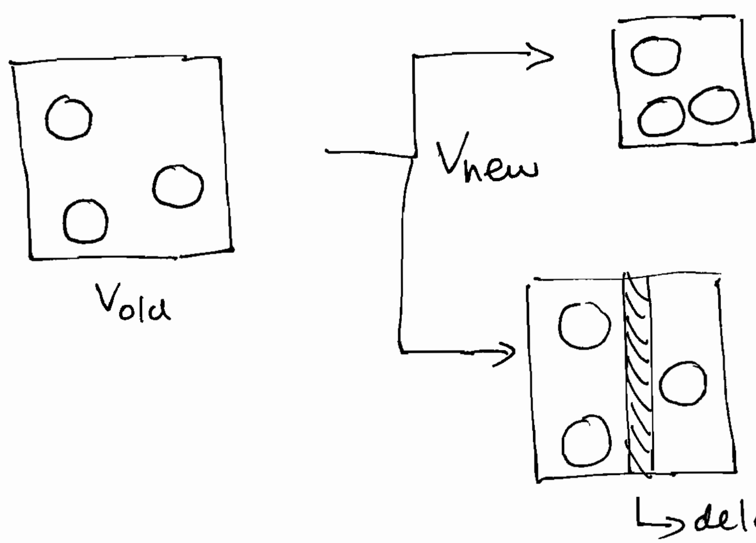
Isothermal-Isobaric MC (NPT)

Most laboratory experiments are carried out at const. pressure and temperature (NPT conditions). The NPT ensemble is often used in computer simulations to obtain equation-of-state data and information on phase transitions.

Probabilities of microstates in NPT ensemble: $P_\nu \propto e^{-\beta U_\nu - \beta P V_\nu}$

How do we change the volume? two options:



- Scale all particle positions
- common choice for continuous potentials

- no scaling;
- good for lattice models

For coordinate scaling, we must take into account ~~that~~ there are more microstates in a bigger volume:

$$\left.\begin{aligned} P_{old} &\propto V_{old}^N \exp(-\beta U_{old} - \beta P V_{old}) \\ P_{new} &\propto V_{new}^N \exp(-\beta U_{new} - \beta P V_{new}) \end{aligned}\right\} \Rightarrow$$

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

assume $\Delta V > 0$, $\Delta V \ll V$

Check for ideal-gas system: $P_{acc}^+ = P_{acc}^- \Rightarrow$

$$\left(\frac{V+\Delta V}{V}\right)^N e^{-\beta P \Delta V} = \left(\frac{V-\Delta V}{V}\right) e^{+\beta P \Delta V} = 1 \Rightarrow 1 + \frac{N\Delta V}{V} = \beta P \Delta V + 1$$

Taylor expand

$\Rightarrow \frac{N}{V} = \rho = \beta P$ ✓ Correct ideal-gas E.O.S.

For volume addition/deletion, no coordinate scaling, so

$$\frac{P_{new}}{P_{old}} = \exp(-\beta \Delta u - \beta P \Delta V)$$

Check for ideal-gas system: $\left\{ P_{acc}^{+} = e^{-\beta P \Delta V} \right.$

$P_{acc}^{-} = 1$, except when removed volume contains particles

$P_{acc}^{+} = P_{acc}^{-} \Rightarrow$

$$e^{-\beta P \Delta V} = \left(1 - \frac{\Delta V}{V}\right)^N$$

$\left(1-\frac{\Delta V}{V}\right)$ is the probability of a single particle not being in ΔV; there are N independent particles

$$\Rightarrow \cancel{1} - \beta P \Delta V = \cancel{1} - \frac{N\Delta V}{V} \Rightarrow \beta P = \rho \;\checkmark$$

Volume changes in $\ln V$

Insted of uniform sampling in V (add/subtract ΔV), which can lead to slow convergence, it is also possible to sample in $\ln V$ (e.g. increase/decrease by up to 5%)

$\Delta V = \Delta V_{max}(2 \cdot \text{rand}() - 1) \rightarrow$ uniform in V

$V_{new} = V_{old} \cdot \exp\left[\ln(\text{factor}) \cdot (2 \cdot \text{rand}() - 1)\right]$ (factor is, e.g., 1.05)

$\rightarrow$ uniform in $\ln V$

For sampling in $\ln V$, the acceptance criterion must

$$d(\ln V) = \frac{1}{V}\,dV \Rightarrow dV = V\,d(\ln V)$$

$$P \propto V^N \cdot V \cdot \exp(-\beta U_V - \beta P V) \Rightarrow \frac{P_{new}}{P_{old}} = \left(\frac{V+\Delta V}{V}\right)^{N+1} \cdot \exp(-\beta \Delta u - \beta P \Delta V)$$

Overall Code Structure

Volume change moves are expensive $(O(N^2))$, while displacement steps are cheap $(O(N))$. **Both** are necessary for equilibration when doing scaling at NPT conditions:

```
for step = 1; Nsteps
    if rand() < prob_dv
        ... volume change ...
    else
        ... displacement ...
    end
end
```

prob_dv typically 1% - 10%, depending on density