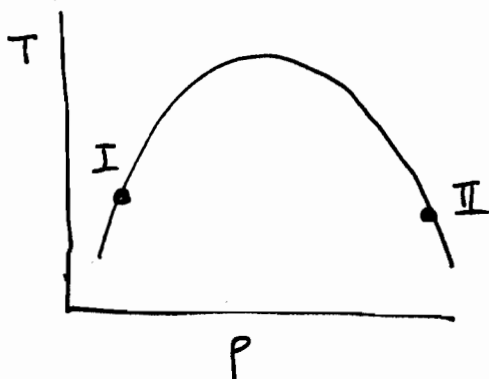


The Gibbs Ensemble

A&P, Molec. Phys. 81, 506 (1987)

for calculations of phase equilibria in a one-component system:

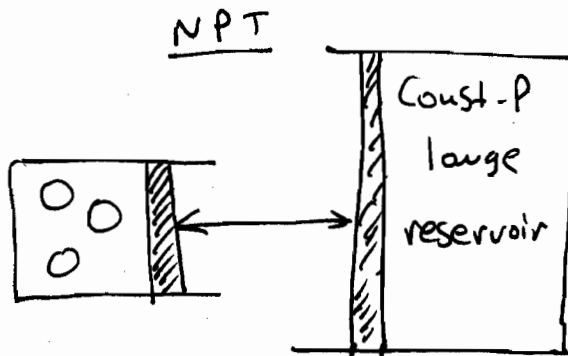
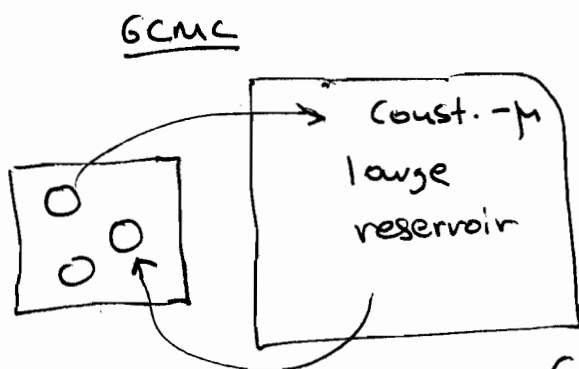


Equil. between phases I and II
@ const. T

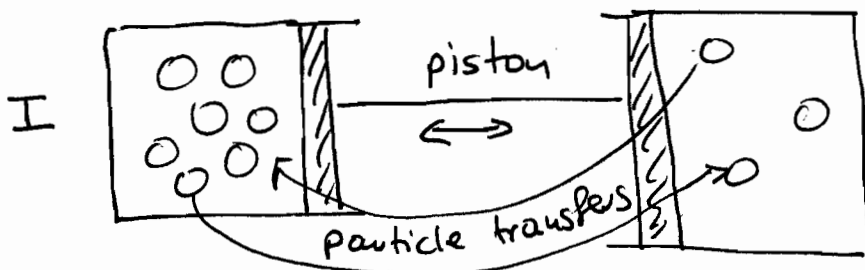
$$\mu^I = \mu^{II}$$

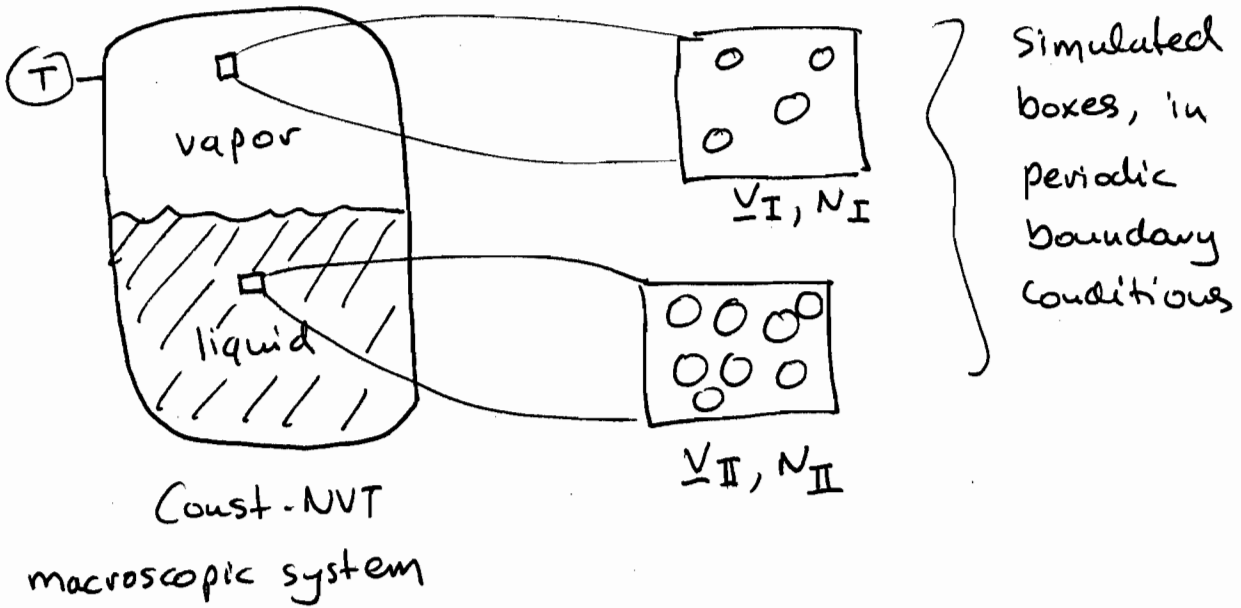
$$p^I = p^{II}$$

In NPT or μ VT simulations, we set the pressure or chemical potential of a system by equilibrating it against an external reservoir:



The key idea of the Gibbs ensemble is to achieve equality of chemical potentials and pressures in the two regions of interest by coupling them:





Probability of a microstate with region I containing N_I particles in volume V_I , region II N_{II} particles in volume $V_{II} \equiv$ (number of microstates of I) \times (number of microstates of II) $\times \exp[-\beta(u_I + u_{II})]$

$$= \frac{1}{N_I!} \cdot V_I^{N_I} \cdot \frac{1}{N_{II}!} \cdot V_{II}^{N_{II}} \cdot \exp(-\beta u_I - \beta u_{II})$$

We need to perform three different types of moves to sample microstates properly:

Displacement moves

$$P_{\text{displace}} = \min [1, \exp(-\beta \Delta u_I - \beta \Delta u_{II})]$$

This is the same as normal NVT simulation in the two boxes. It is more efficient to perform displacement moves separately in each region.

Control acceptance of displacement moves by changing Δr_{max} to achieve acceptance of $\sim 30\% - 50\%$

Volume Changes

$$\underline{V}_I \rightarrow \underline{V}_I + \Delta V$$

$$\underline{V}_{II} \rightarrow \underline{V}_{II} - \Delta V$$

$$P_{\text{volume}} = \min \left[1, \left(\frac{\underline{V}_I + \Delta V}{\underline{V}_I} \right)^{N_I} \cdot \left(\frac{\underline{V}_{II} - \Delta V}{\underline{V}_{II}} \right)^{N_{II}} \cdot \exp(-\beta(\Delta u_I + \Delta u_{II})) \right]$$

In many cases, one of the two regions has a much smaller density than the other (e.g. vapor at equilibrium with liquid). Since we want a "reasonable" number of particles in both phases, we must have $\underline{V}_{\text{vapor}} \gg \underline{V}_{\text{liquid}}$, so acceptance of volume changes is controlled by the liquid.

Particle Transfers

$$N_{II} \rightarrow N_{II} - 1$$

$$N_I \rightarrow N_I + 1$$

for transfer of a particle from region II to region I.

$$P_{\text{transfer}} = \min \left[1, \exp(-\beta \Delta u_I - \beta \Delta u_{II}) \times \frac{N_{II}}{\underline{V}_{II}} \times \frac{\underline{V}_I}{N_I + 1} \right]$$

Particle transfer steps can have very low acceptance probabilities for dense phases, which limits the practical applicability of the Gibbs ensemble method in its original form.

Ratios of moves

To satisfy detailed balance, the move type must be decided at random with fixed probabilities. Typical

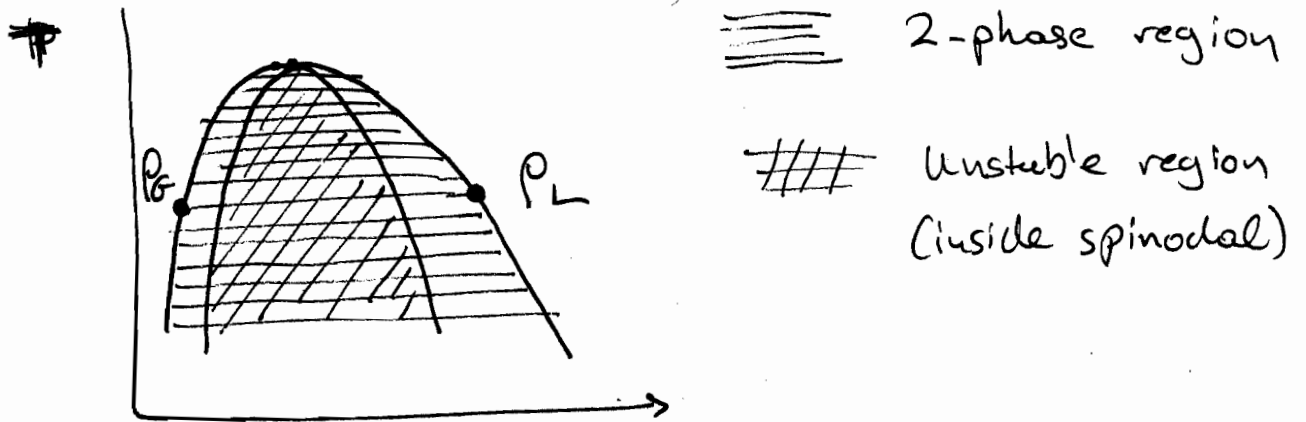
ratios are

$$\text{displacement} : \text{volume change} : \text{transfer} = 100 : 1 : 200$$

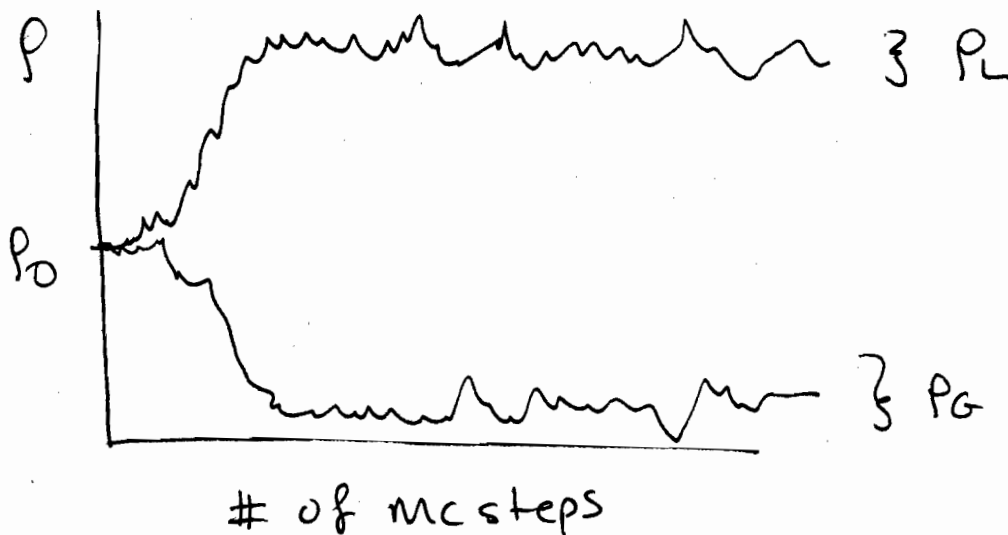
The ratio of attempted transfers to overall moves is determined by the need to have a "reasonable" number of successful transfers ($> 1,000$) over a simulation run.

Starting Condition

22-141 50 SHEETS
22-142 100 SHEETS
22-144 200 SHEETS
AMPSO



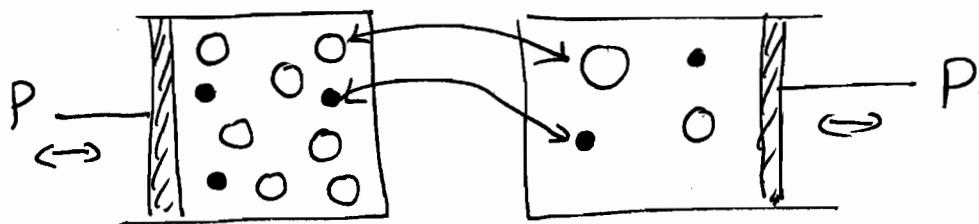
A system with initial density ρ in the unstable region quickly phase separates to reduce its overall free energy - same as in lab experiment:



Mixtures

The method can be applied in the same form to multicomponent mixtures. The particle transfer step applies to each component separately.

For mixtures, there are additional degrees of freedom that allow simulations at constant- P :

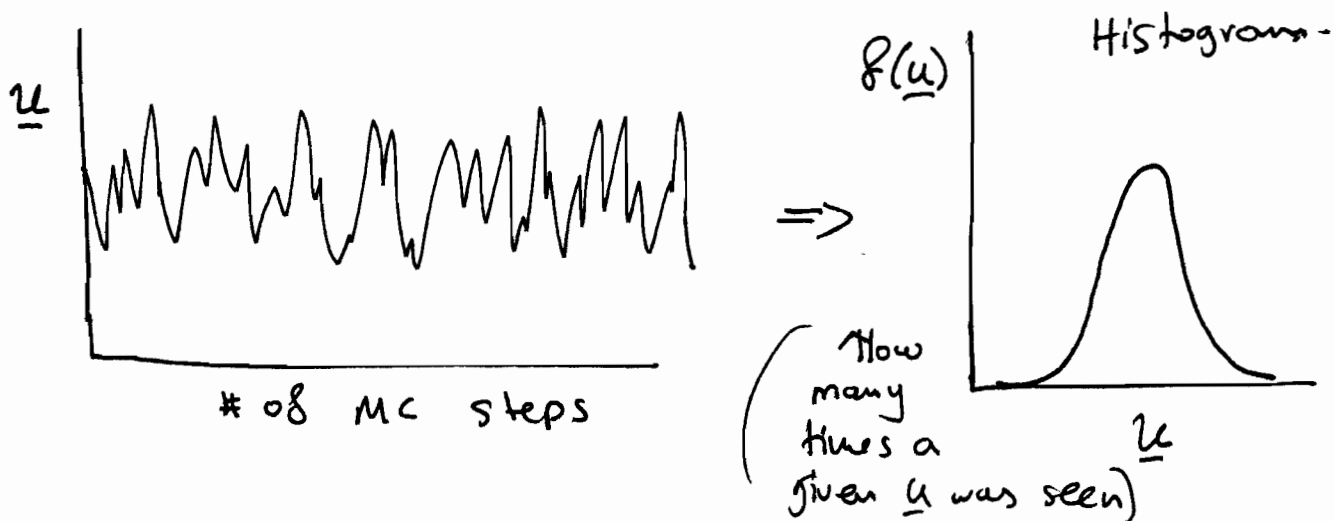


transfer of
both components

For const- P Gibbs ensemble simulations,

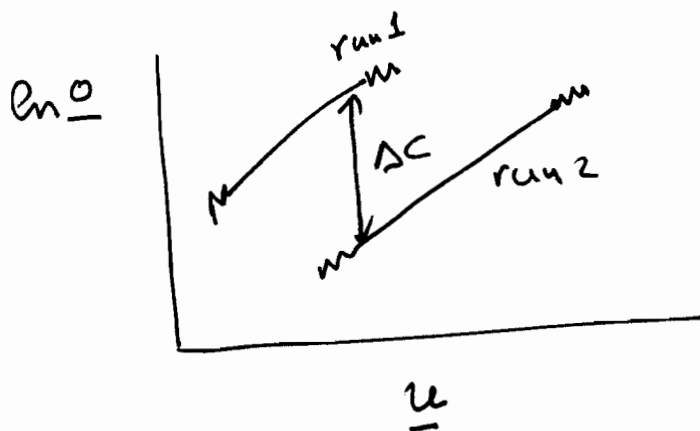
$$P_{\text{volume}} = \min \left[1, \left(\frac{V_{\text{I}} + \Delta V_{\text{I}}}{V_{\text{I}}} \right)^{N_{\text{I}}} \left(\frac{V_{\text{II}} + \Delta V_{\text{II}}}{V_{\text{II}}} \right)^{N_{\text{II}}} \cdot \exp \left[-\beta \Delta U - P(\Delta V_{\text{I}} + \Delta V_{\text{II}}) \right] \right]$$

(For pure components, the vapor pressure is not a degree of freedom at constant T)

Histogram Reweightinge.g. NVT ensemble simulation

$$f(u) \propto \Omega(N, u, V) \cdot \exp(-\beta u) \Rightarrow$$

$$\ln f(u) + \beta u = \ln \Omega(N, u, V) + \underbrace{C}_{\text{unknown constant}}$$



Determine ΔC to produce "global" $\Omega(u)$ curve

Same way μVT simulations $\Rightarrow f(u, N) \text{ vs } u, \mu$

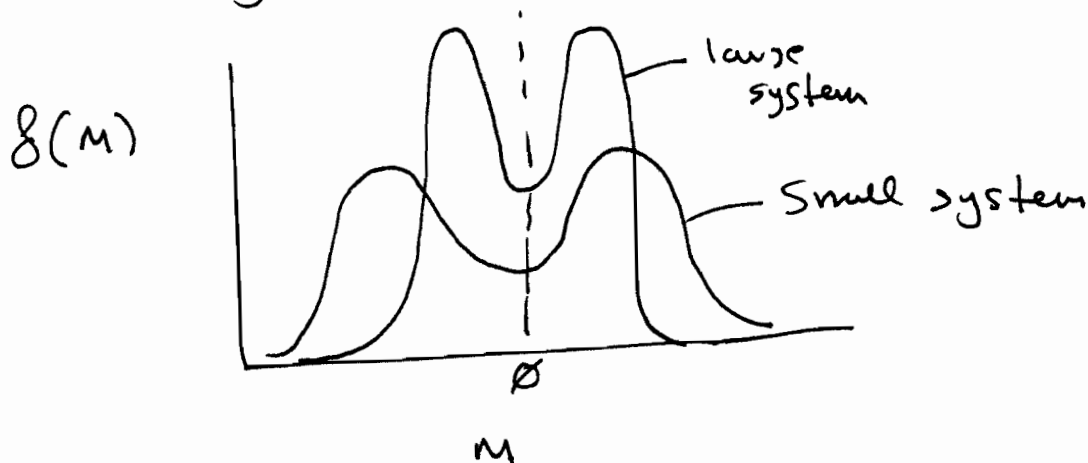
$$\ln(f(u, N)) + \beta u - \beta \mu N = \ln \Omega(N, V, u) + \underline{C}$$

\Rightarrow can be used for phase equl, T_c , PVT equations ^{unknown}

Mixed field Finite-size scaling

GMC / histogram methods are particularly useful near critical points

For Ising model at $T = T_c$



For fluids $M = N + s \underline{u}$ (mixed $N + \underline{u}$)
 \hookrightarrow field mixing parameter

At system critical point, universal form of normalized $g(M)$ distribution