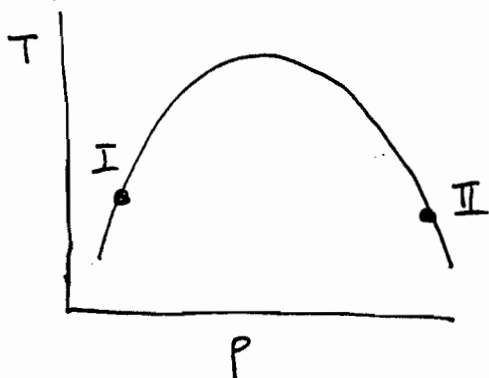


The Gibbs Ensemble

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

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

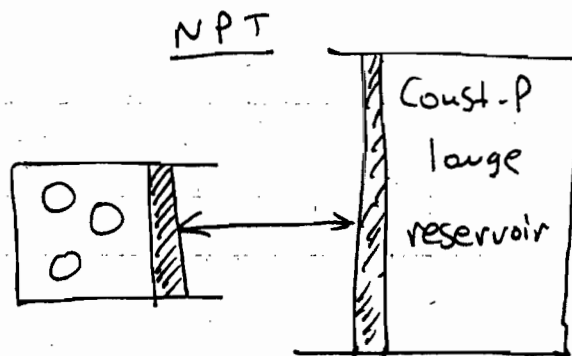
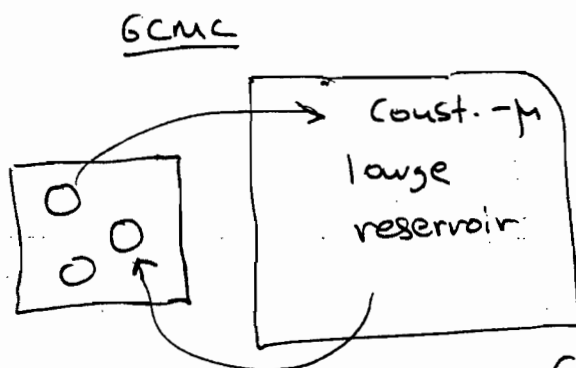


Equil. between phases I and II
@ const. T

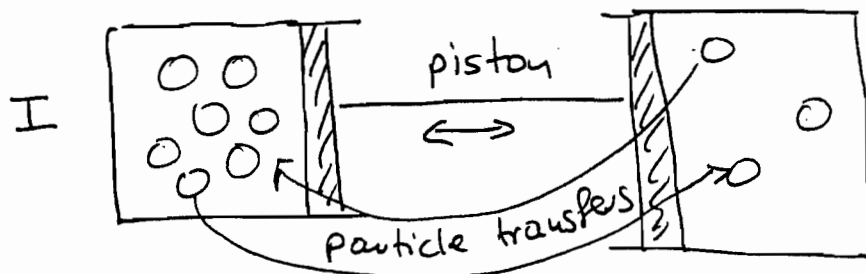
$$\mu^I = \mu^II$$

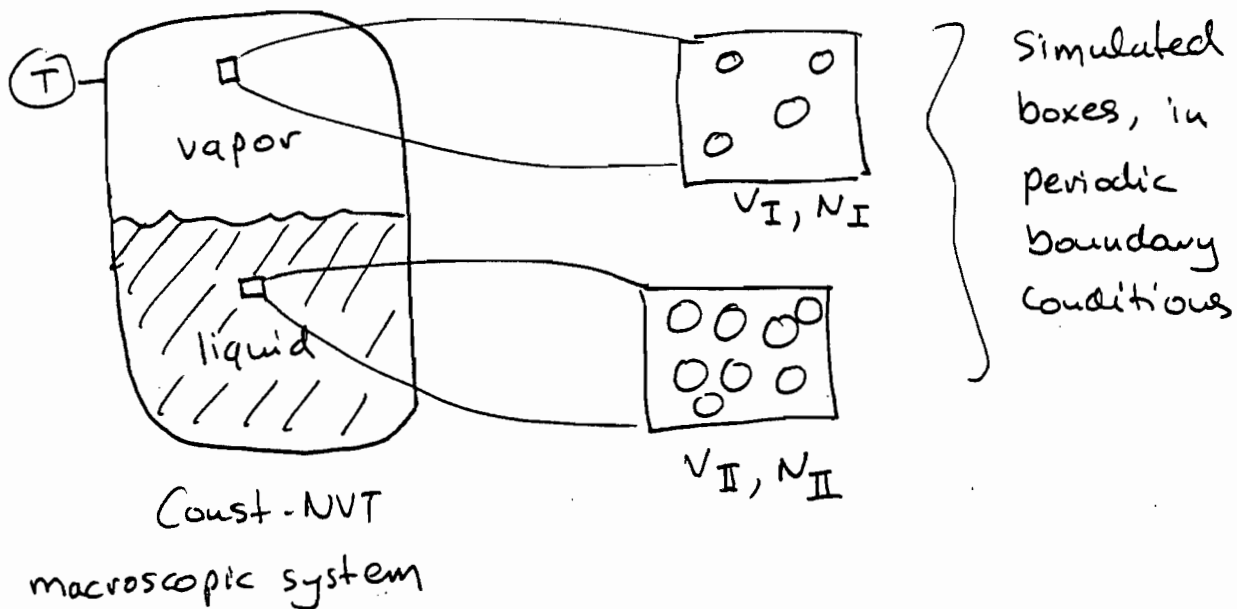
$$p^I = p^II$$

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} = (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 $\sim 30\% - 40\%$

Volume Changes

$$V_I \rightarrow V_I + \Delta V$$

$$V_{II} \rightarrow V_{II} - \Delta V$$

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

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 $V_{\text{vapor}} \gg V_{\text{liquid}}$, 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.

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

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

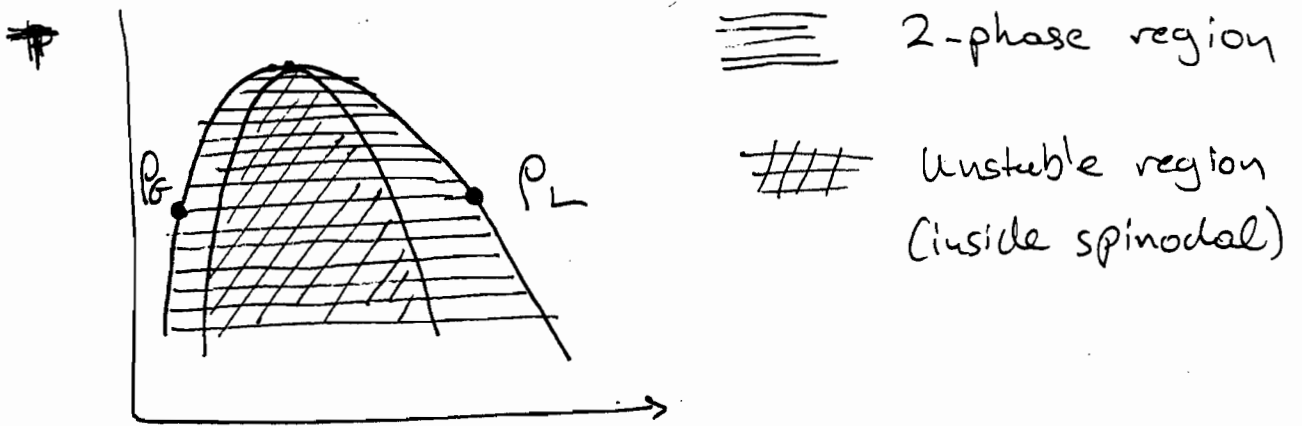
To satisfy detailed balance, the move type must be decided at random with fixed probabilities. Typical

ratios are

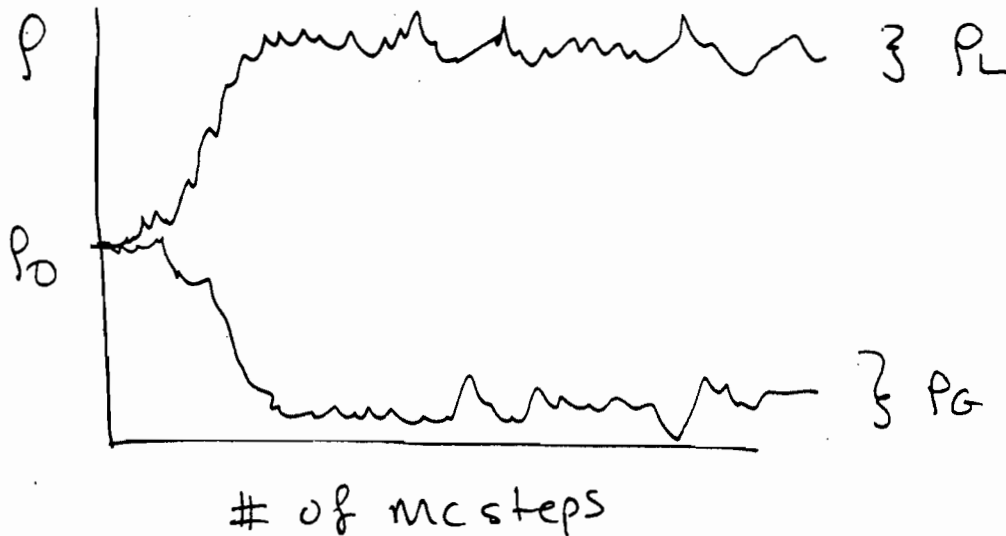
displacement : volume change : transfer = 100 : 1 : 200

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



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

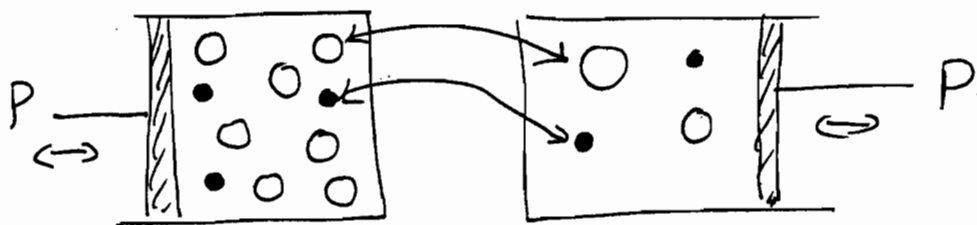


50 SHEETS
22-141
100 SHEETS
22-142
200 SHEETS
22-144
ANIPAD

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,

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

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

Implementation

Gibbs ensemble simulations usually run in cycles of attempted displacements, volume changes, particle transfers.

p_{displ}
 p_{volume} } Cumulative probabilities $0 < p_{\text{displ}} < p_{\text{volume}} < 1$
 $p_{\text{transfer}} = 1 - p_{\text{volume}}$

do cycle = 1, ncycle

move = rand()

if (move < p_{displ}) then

call displace(-----) ← (displace attempt in each of the regions)

else if (move < p_{volume}) then

call volume(---)

else

call transfer(---) ← (I → II or II → I w/ equal prob.)

if (modulo (cycle, nsample) == 0) &

call sample(--) ← printout properties

Enddo

Pressure + Chemical Potential Calculation

P and μ can be calculated in the usual way
 (P : virial or "test volume" additions/removals)
 (μ : widow insertions)

It is a good idea to check that they are indeed equal (within statistical uncertainties) in the 'production' period.

Which method is better?

GCMC/Histograms or Gibbs ensemble?

It depends...

- (a) Near critical points, Gibbs ensemble fails because there is no driving force for keeping phases separate
- (b) For generating complete/high accuracy phase diagrams over broad temperature range, GCMC/Histograms has the advantage
- (c) If a few deeply subcritical points are of interest, Gibbs has the advantage

E.g. Paluch, Shen + Errington, IEC Research, 47:4533 (2008)

