

Grand Canonical (μVT) MC

Contrary to lab experiments (which cannot easily be done in this fashion, except when there are semi-permeable membranes in a system) simulations can be easily performed under constant chemical potential conditions. These calculations are very important for phase equilibrium calculations.

Fundamental Equation: $k_B d\ln \Omega = dS = \frac{1}{T} du + \frac{P}{T} dv - \frac{\mu}{T} dN$

NVT - ensemble: $k_B d\ln \Omega = d\left(-\frac{A}{T}\right) = -u d\left(\frac{1}{T}\right) + \frac{P}{T} dv - \frac{\mu}{T} dN$

μVT - ensemble: $k_B d\ln \Xi = d\left(\frac{PV}{T}\right) = -u d\left(\frac{1}{T}\right) + Nd\left(\frac{\mu}{T}\right) + \frac{P}{T} dv$

$$y^{(2)} = \ln \Xi = \frac{S}{k_B} - \beta u + \beta \mu N = \frac{PV}{k_B T}$$

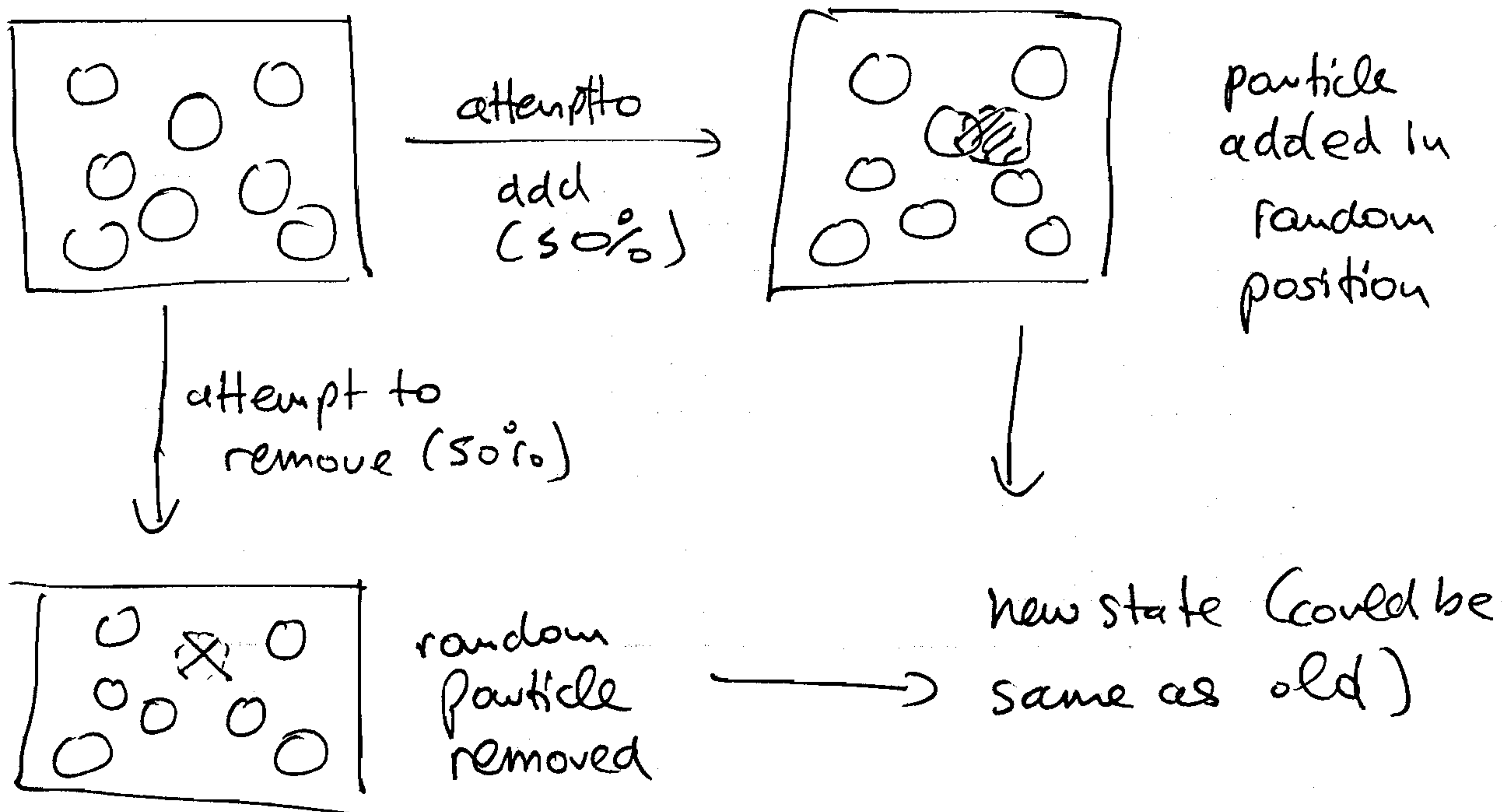
$$\Xi = \sum_{\text{all microstates}} \exp(-\beta u_v + \beta \mu N_v) \left. \begin{array}{l} u_v, \\ N_v \end{array} \right\} \text{fluctuate}$$

$$P_v = \frac{\exp(-\beta u_v + \beta \mu N_v)}{\Xi} \left(\frac{\partial \ln \Xi}{\partial \beta \mu} \right)_{\beta, V} = \langle N \rangle$$

Fluctuations: $\langle (\delta N)^2 \rangle = k_B T^2 \left(\frac{\partial N}{\partial \mu} \right)_{T, V}$

diverges at phase transition

To change the number of particles, we need to try particle additions and removals:



for addition: $\text{Accept}(N \rightarrow N+1) =$

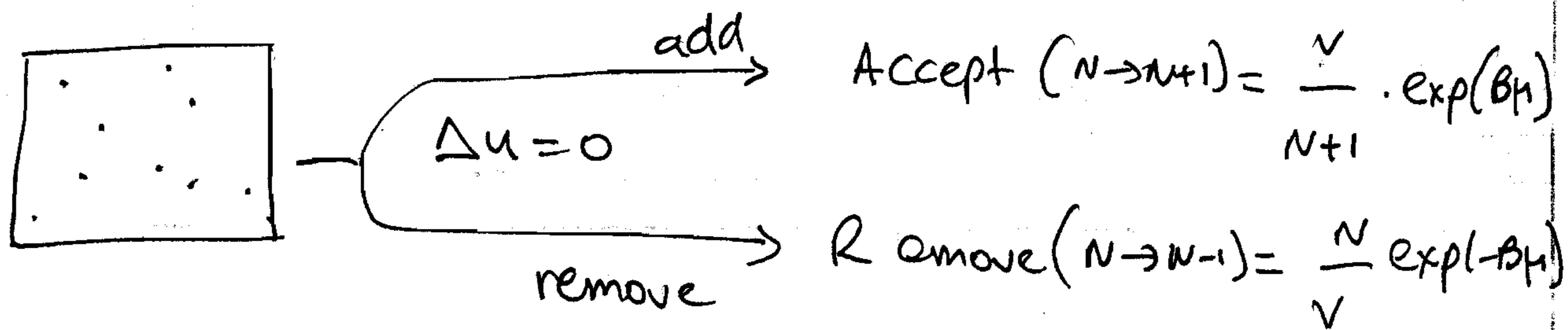
$$= \frac{\frac{V^{N+1}}{(N+1)!} \cdot P_{N+1}}{\frac{V^N}{N!} P_N} = \frac{V}{N+1} \cdot \exp(-\beta \Delta u + \beta \mu)$$

The term $\frac{V^{N+1}}{(N+1)!}$ appears because there are V^{N+1} states and $(N+1)$ indistinguishable particles - will show that it is correct for ideal gases.

for removal, same way: $\text{Accept}(N \rightarrow N-1) =$

$$= \frac{\frac{V^{N-1}}{(N-1)!} P_{N-1}}{\frac{V^N}{N!} P_N} = \frac{N}{V} \cdot \exp(-\beta \Delta u - \beta \mu)$$

Let's try again a thought experiment in which we perform a GCMC simulation for an ideal gas.



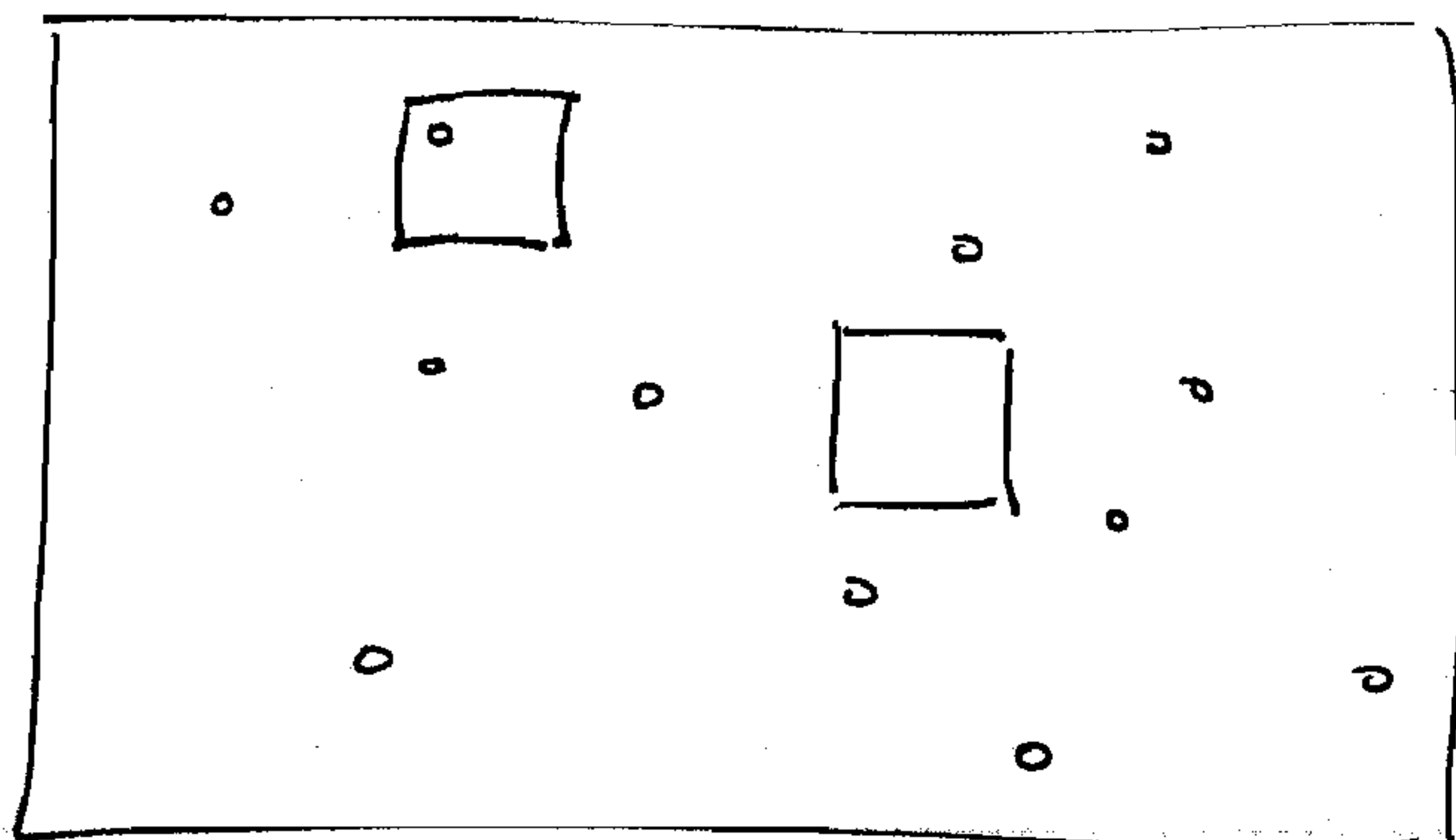
The two terms are inverse of each other, so only one is less than one. At equilibrium, the two must be equal, so that

$$\frac{N}{V} \exp(-\beta\mu) = 1 \Rightarrow \beta\mu = \ln \frac{N}{V} = \ln \rho \Rightarrow$$

$$\boxed{\mu = kT \ln \rho}$$

which is the correct expression for the chemical potential of an ideal gas!

Note that the acceptance relationships allow for a box to become empty ($N=0$) \rightarrow nothing "blows up" - this is correct, as in a certain volume at low densities it is possible that there are no particles:



large system at low density

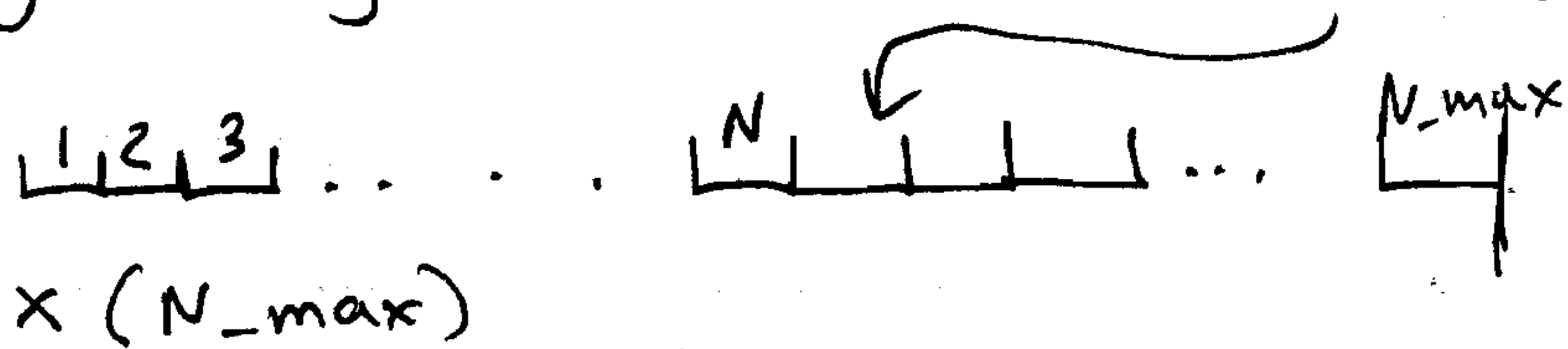
: Small simulation box

Implementation Issues

Acceptance of insertion/removal steps cannot be controlled. It can be very low at high densities.

In such cases, one needs to try out a large number of attempted insertions/deletions relative to other moves (e.g. displacements). Actually, displacements are in principle not necessary to equilibrate the system, as insertions/deletions move particles around.

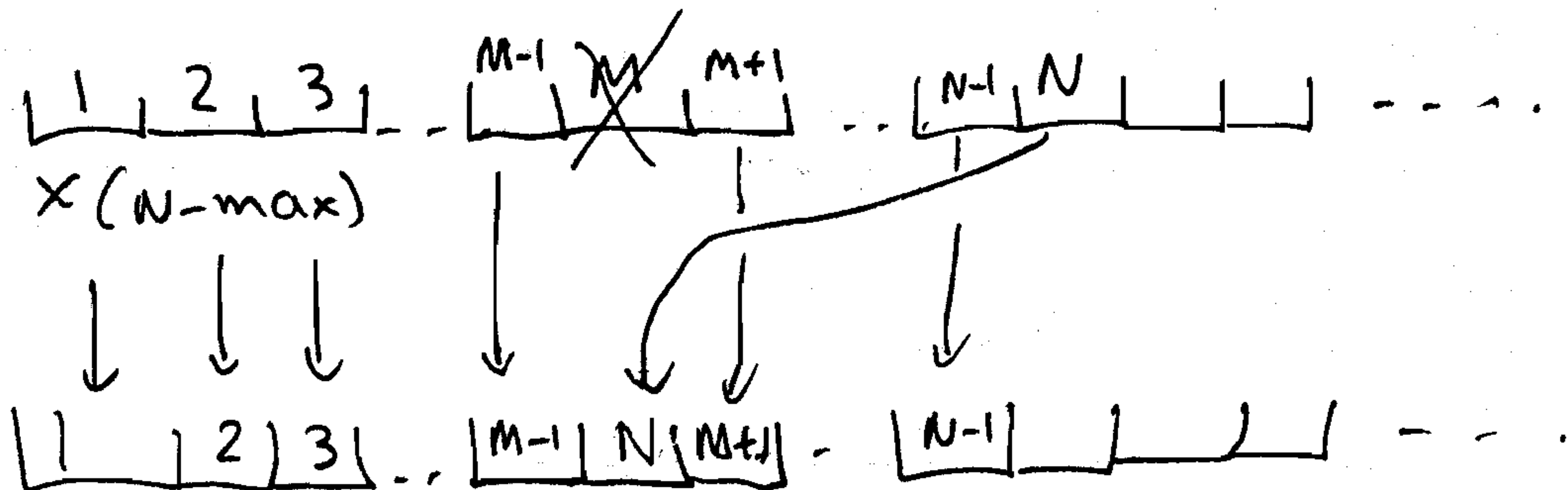
Rearrangement of position vectors: On successful insertion, the "active" dimension of position arrays grows by one: $(N+1)$ particle



If $(N+1) > N_{max}$ then
write $(*)$...
stop
end if
 $X(N+1) = X_{new}$
 $N = N+1$

$N_{max} \geq N$ at all times!

For successful deletion, need to "patch" hole:



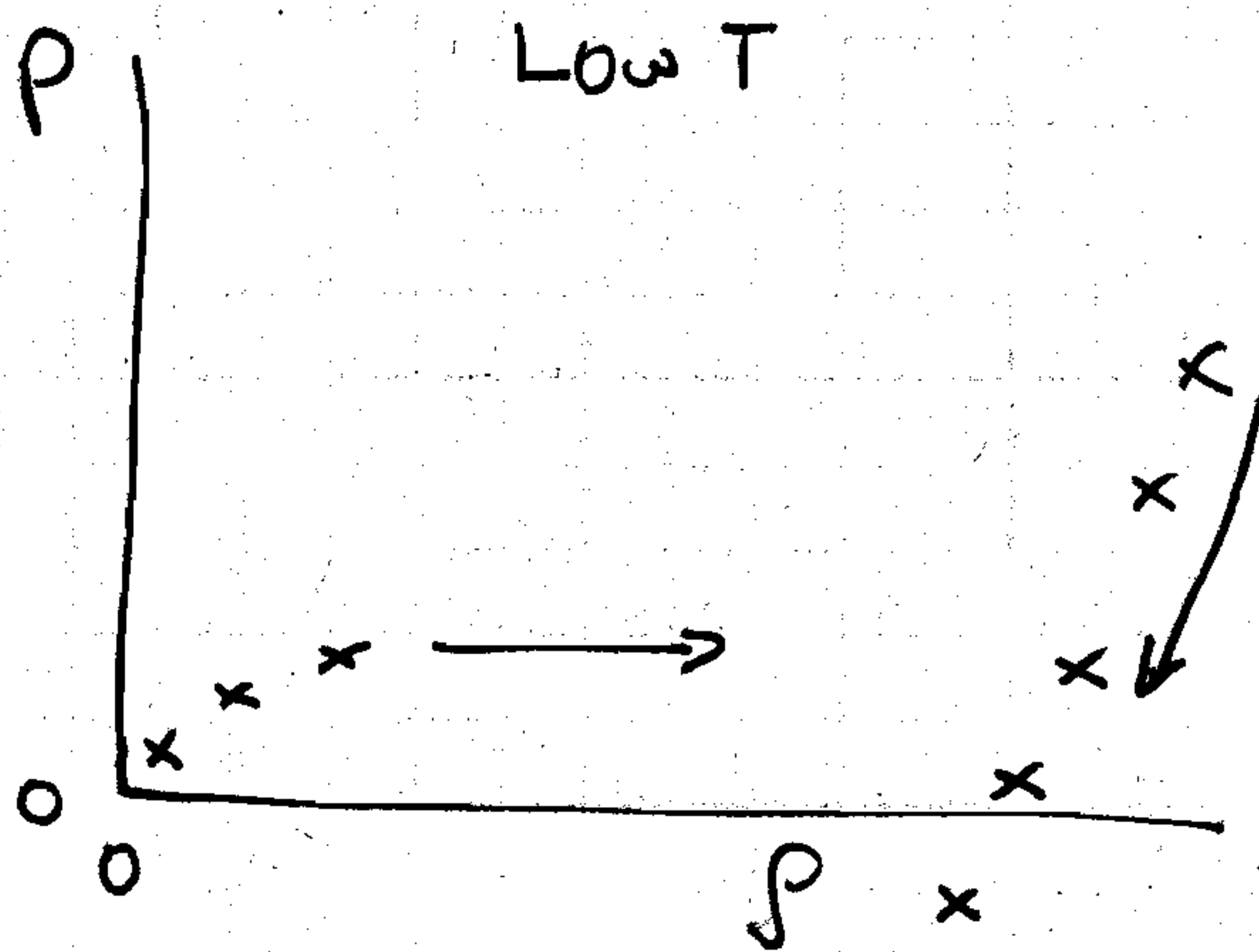
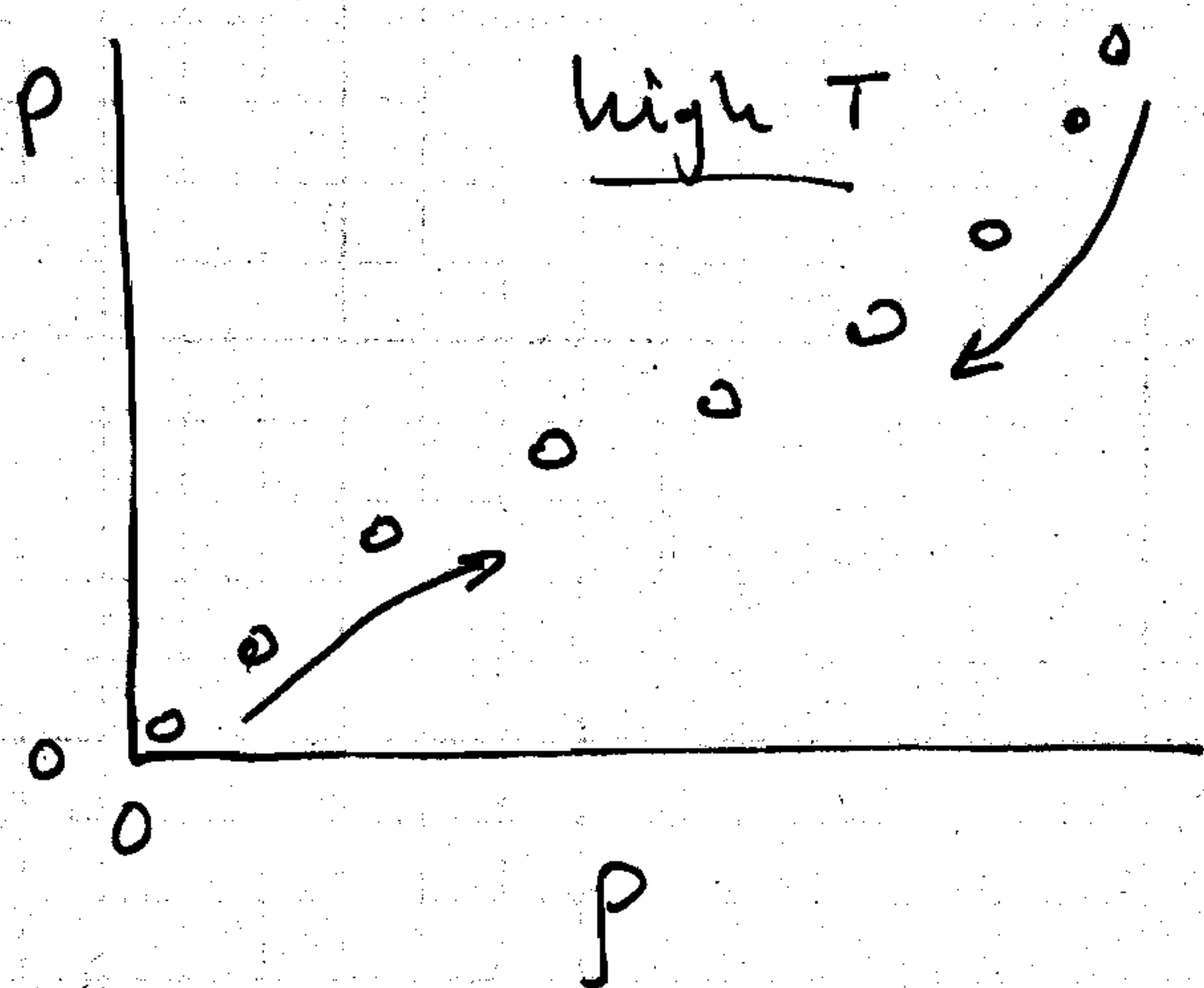
$X(N_{max})$

$X(M) = X(N)$

$N = N-1$

Metastable States

In GCMC or NPT ensemble calculations, you are likely to observe the following behavior at some temperatures:



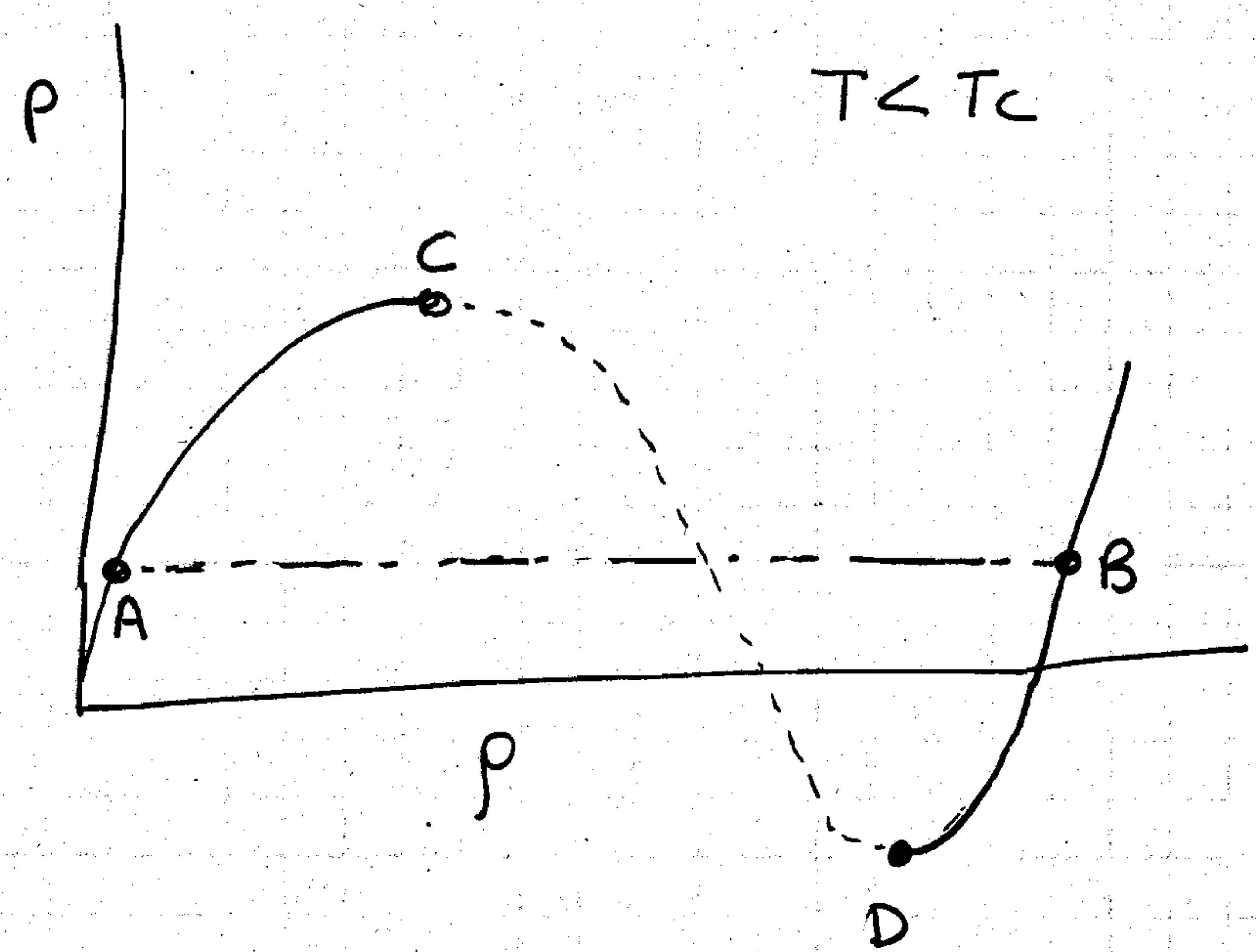
At high temperatures, it does not matter if your initial density is low or high, you always get (roughly) the same answer for $\rho(P)$. At low temperatures, however, if you start from a low-density initial configuration, as pressure increases density increases and then "jumps" to a high value. From this state, when you decrease the pressure, the density stays high, even if the imposed pressure gets negative!

This "hysteresis" is associated with phase transitions. It is observed experimentally (e.g. in bubble chambers, in clouds or when you place "boiling stones" in liquids you want to boil in an organic chemistry lab.)

Even though there are states of lower free energy, a simulated (or real) system cannot overcome the free

energy "nucleation" barrier to go over to the other state. The barrier is higher at lower temperatures.

This feature is also present for equations-of-state (e.g. vdw equation, $P = \frac{RT}{v-b} - \frac{a}{v^2}$)



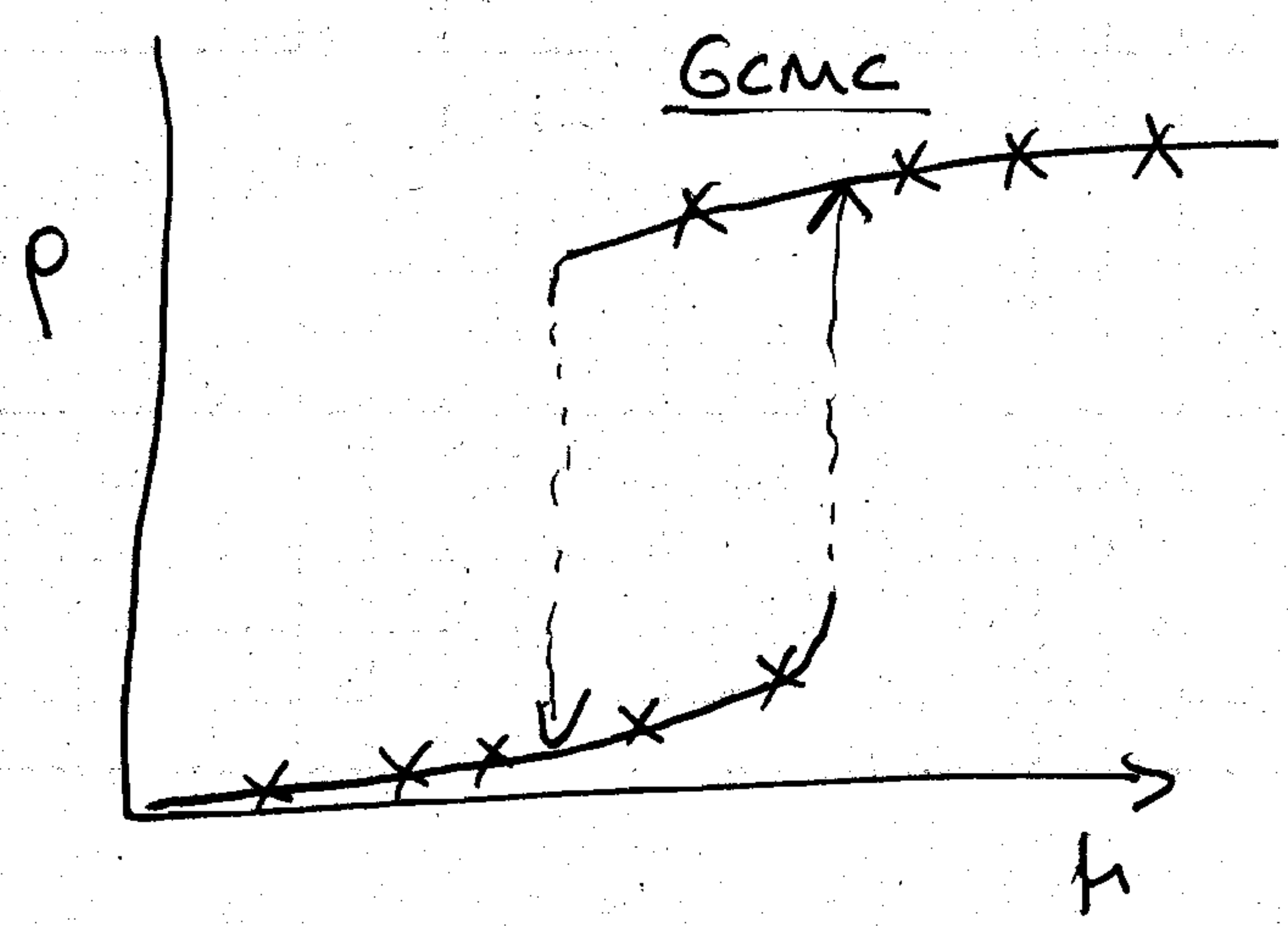
A, B: equilibrium points (from Maxwell const.)

C, D: limits of stability

$$\left. \frac{\partial P}{\partial v} \right|_T = 0$$

AC & DB: metastable segments

For the simulations, one cannot perform an equal-area (Maxwell) construction, so there is uncertainty in the exact location of the phase transition if just NPT simulations are performed. NPT simulations need to be combined with GCMC to get the correct (equilibrium) densities of the transition:



Solve for

$$\mu(p^I) = \mu(p^{II})$$

$$P(p^I) = P(p^{II})$$

(hard to do, many simulations needed)