Monte Carlo in different ensembles
Chapter 5

NVT ensemble
NPT ensemble
Grand-canonical (μVT) ensemble
Exotic ensembles: semigrand, isotension

Different Ensembles

Ensemble	Name	Constant (Imposed)	Fluctuating (Measured)	Thermo-dynamics
NVT	Canonical	N,V,T	P	F
NPT	Isobaric-isothermal	N,P,T	V	G
μVT	Grand-canonical	μ,V,T	N	Ω

NVT ensemble: Statistical Thermodynamics

Partition function

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathrm{r}^N \exp\left[-\beta U\left(\mathrm{r}^N\right)\right]$$

Ensemble average

$$\left\langle A \right\rangle_{NVT} = \frac{1}{Q_{NVT}} \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathrm{r}^N A\left(\mathrm{r}^N\right) \exp\left[-\beta U\left(\mathrm{r}^N\right)\right]$$

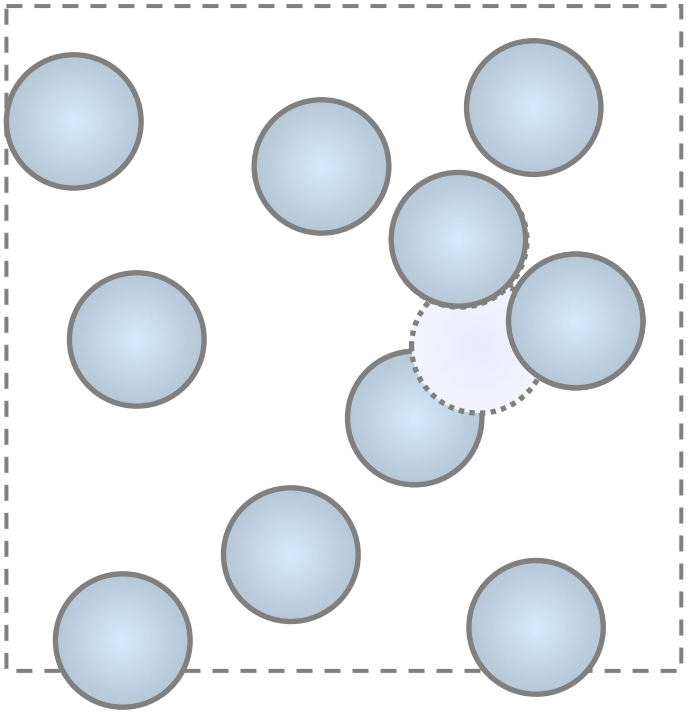
Probability to find a particular configuration

$$\mathrm{N}\left(\mathrm{r}^N\right) = \frac{1}{Q_{NVT}} \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathrm{r}'^N \delta\left(\mathrm{r}'^N - \mathrm{r}^N\right) \exp\left[-\beta U\left(\mathrm{r}'^N\right)\right] \propto \exp\left[-\beta U\left(\mathrm{r}^N\right)\right]$$

Free energy

$$\beta F = -\ln\left(Q_{NVT}\right)$$

Monte Carlo sampling



Monte Carlo simulation

Samples configuration space according to the Boltzmann distribution

$$\langle A \rangle = \frac{\int dr^N \, A \, e^{-U(r^N)/k_B T}}{\int dr^N \, e^{-U(r^N)/k_B T}}$$

Ensemble average

$$\langle A \rangle_{NVT} = \frac{1}{Q_{NVT}} \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) \exp\left[-\beta U(\mathbf{r}^N)\right]$$

$$= \int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) P(\mathbf{r}^N) \quad = \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) P(\mathbf{r}^N)}{\int \mathrm{d}\mathbf{r}^N P(\mathbf{r}^N)}$$

$$P(\mathbf{r}^N) = \frac{\exp\left[-\beta U(\mathbf{r}^N)\right]}{Q_{NVT} \Lambda^{3N} N!}$$

$$= \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) C \exp\left[-\beta U(\mathbf{r}^N)\right]}{\int \mathrm{d}\mathbf{r}^N C \exp\left[-\beta U(\mathbf{r}^N)\right]} \quad = \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) \exp\left[-\beta U(\mathbf{r}^N)\right]}{\int \mathrm{d}\mathbf{r}^N \exp\left[-\beta U(\mathbf{r}^N)\right]}$$

Generate configuration using MC:

$$\left\{\mathbf{r}_1^N, \mathbf{r}_2^N, \mathbf{r}_3^N, \mathbf{r}_4^N \cdots, \mathbf{r}_M^N\right\}$$

$$\overline{A} = \frac{1}{M} \sum_{i=1}^{M} A(\mathbf{r}_i^N) \approx \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) P^{MC}(\mathbf{r}^N)}{\int \mathrm{d}\mathbf{r}^N P^{MC}(\mathbf{r}^N)}$$

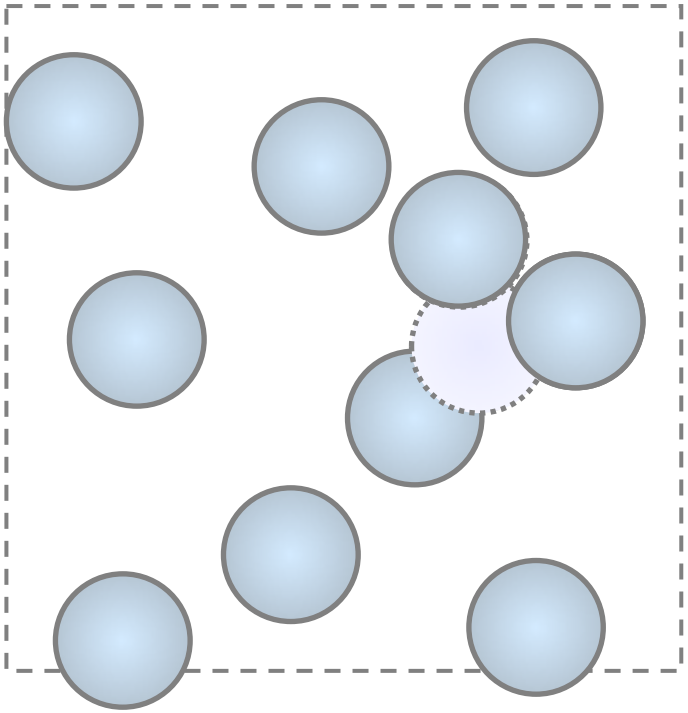
with

$$P^{MC}(\mathbf{r}^N) = C^{MC} \exp\left[-\beta U(\mathbf{r}^N)\right]$$

$$= \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) C^{MC} \exp\left[-\beta U(\mathbf{r}^N)\right]}{\int \mathrm{d}\mathbf{r}^N C^{MC} \exp\left[-\beta U(\mathbf{r}^N)\right]}$$

$$= \frac{\int \mathrm{d}\mathbf{r}^N A(\mathbf{r}^N) \exp\left[-\beta U(\mathbf{r}^N)\right]}{\int \mathrm{d}\mathbf{r}^N \exp\left[-\beta U(\mathbf{r}^N)\right]}$$

Monte Carlo sampling



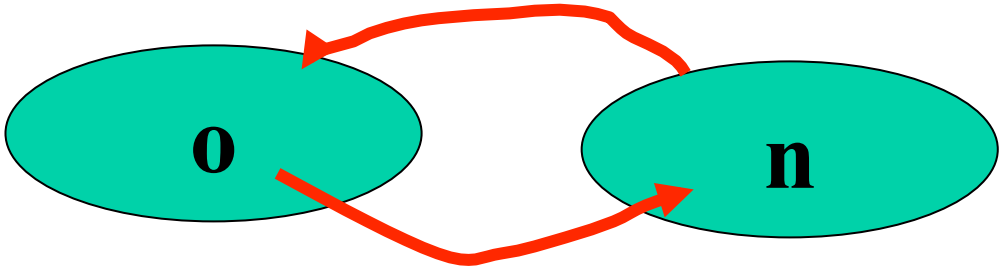
Monte Carlo simulation

Samples configuration space according to the Boltzmann distribution

$$\langle A \rangle = \frac{\int dr^N A\, e^{-U(r^N)/k_B T}}{\int dr^N\, e^{-U(r^N)/k_B T}}$$

How do we derive monte carlo algorithm?

Detailed balance



$$K(o \to n) = K(n \to o)$$

$$K(o \to n) = N(o) \times \alpha(o \to n)$$

$$K(n \to o) = N(n) \times \alpha(n \to o)$$

Symmetric generation probability

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n) \times \alpha(n \to o)}{N(o) \times \alpha(o \to n)} = \frac{N(n)}{N(o)}$$

NVT-*ensemble*

$$N(n) \propto \exp\left[-\beta U\left(n\right)\right]$$

$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{N(n)}{N(o)}$$

$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \exp\left[-\beta\left[U\left(n\right) - U\left(o\right)\right]\right]$$

Choice of metropolis et al.

$$\mathrm{acc}(o \rightarrow n) = \min\left[1, \exp(-\beta \Delta U(o \rightarrow n)\right]$$

Algorithm 2 (Attempt to Displace a Particle)

```
      SUBROUTINE mcmove                attempts to displace a particle

      o=int(ranf()*npart)+1            select a particle at random
      call ener(x(o),eno)              energy old configuration
      xn=x(o)+(ranf()-0.5)*delx        give particle random displacement
      call ener(xn,enn)                energy new configuration
      if (ranf().lt.exp(-beta          acceptance rule (3.2.1)
     +    *(enn-eno)) x(o)=xn          accepted: replace x(o) by xn
      return
      end
```

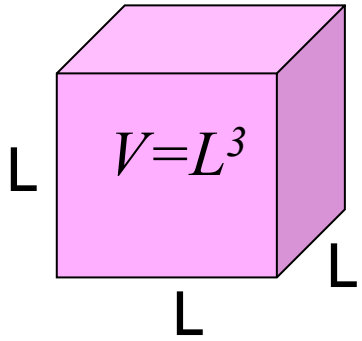
Comments to this algorithm:

1. *Subroutine* `ener` *calculates the energy of a particle at the given position.*
2. *Note that, if a configuration is rejected, the old configuration is retained.*
3. *The* `ranf()` *is a random number uniform in* $[0, 1]$.

Scaled coordinates

Partition function

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{r}^N \exp\left[-\beta U\left(\mathbf{r}^N\right)\right]$$



Scaled coordinates

$$\mathbf{s}_i = \mathbf{r}_i / L$$

The energy depends on the real coordinates

This gives for the partition function

$$Q_{NVT} = \frac{L^{3N}}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{s}^N \exp\left[-\beta U\left(\mathbf{s}^N; L\right)\right]$$

$$= \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{s}^N \exp\left[-\beta U\left(\mathbf{s}^N; L\right)\right]$$

Measuring the pressure

The pressure is the thermodynamic derivative of F

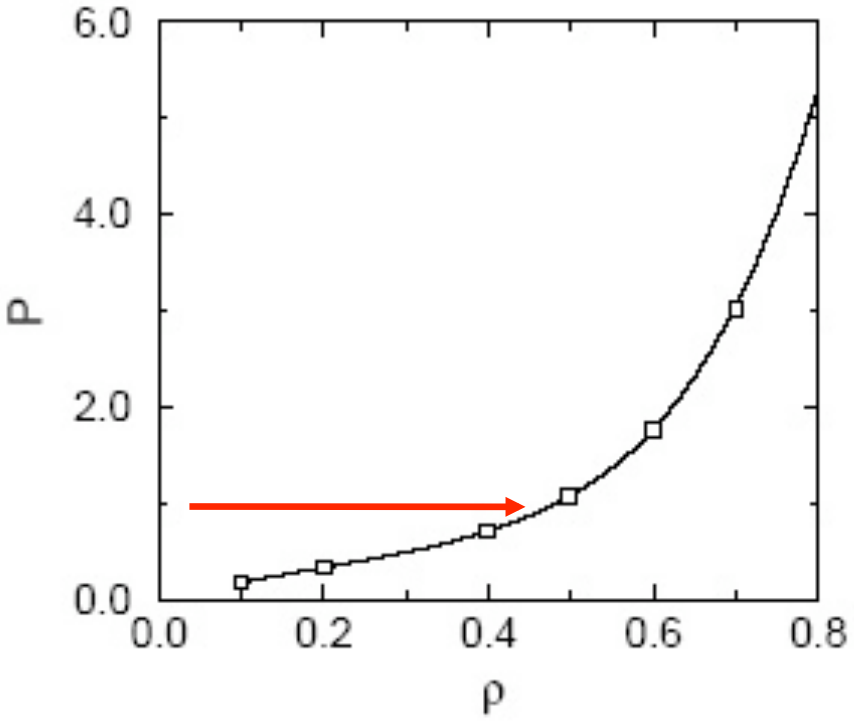
$$\beta P = -\left(\frac{\partial \beta F}{\partial V}\right)_{N,T} = \left(\frac{\partial \ln Q_{NVT}}{\partial V}\right)_{N,T} = \frac{1}{Q_{NVT}}\left(\frac{\partial Q_{NVT}}{\partial V}\right)_{N,T}$$

$$= \frac{\frac{NV^{N-1}}{\Lambda^{3N} N!}\int ds^N e^{-\beta U(r^N)} - \frac{V^N}{\Lambda^{3N} N!}\int ds^N e^{-\beta U(r^N)} \frac{d\beta U(r^N)}{dV}}{\frac{V^N}{\Lambda^{3N} N!}\int ds^N e^{-\beta U(s^N)}}$$

this reduces to the virial pressure

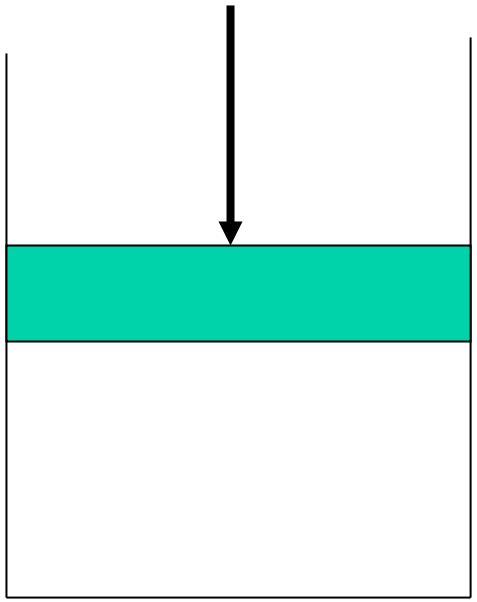
$$\beta P = \rho - \left\langle \frac{d\beta U(r^N)}{dV} \right\rangle$$

Constant pressure simulation?



- what if we are interested in one specific pressure P?
- we need large part of the equation of state to find right volume V
  - needs many simulations.
- Better idea: constant pressure simulation.

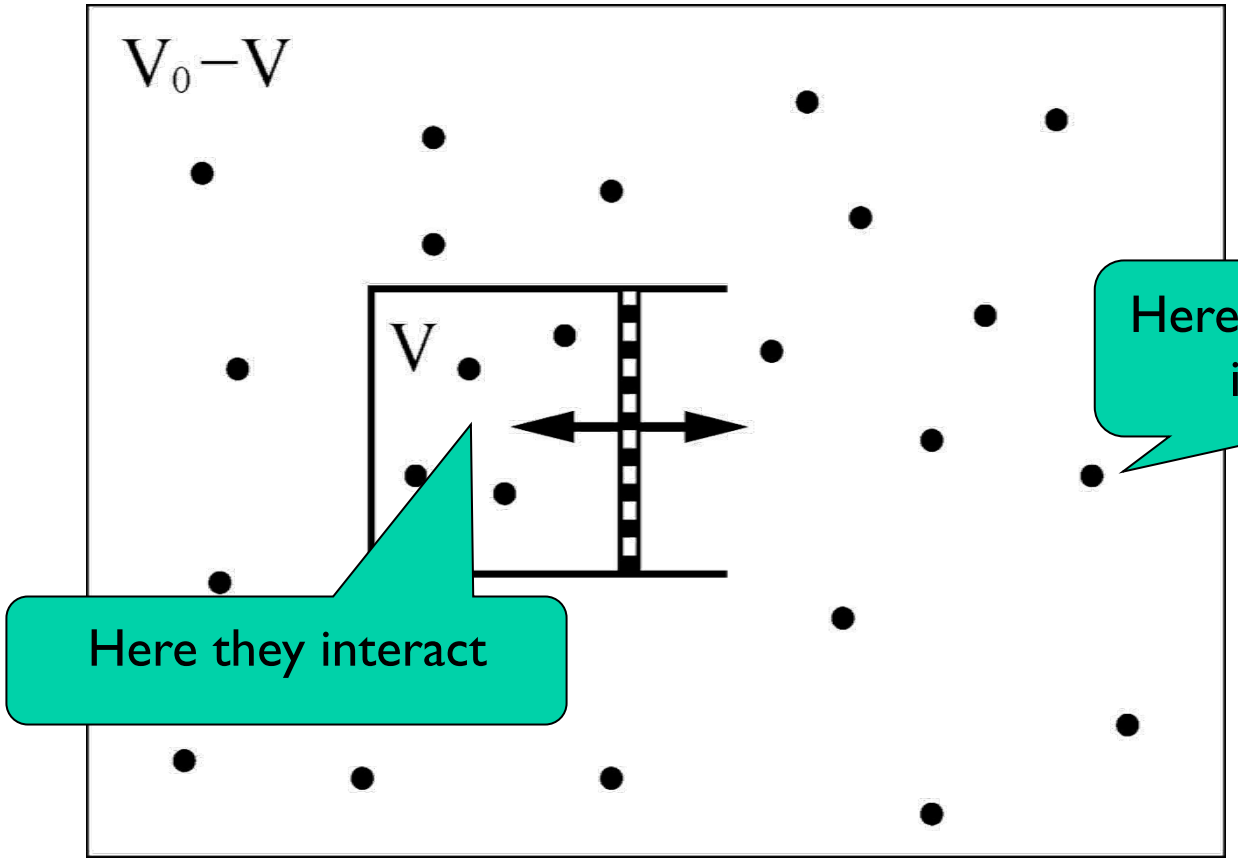
NPT ensemble



We control the

- Temperature (T)
- Pressure (P)
- Number of particles (N)

The perfect simulation ensemble

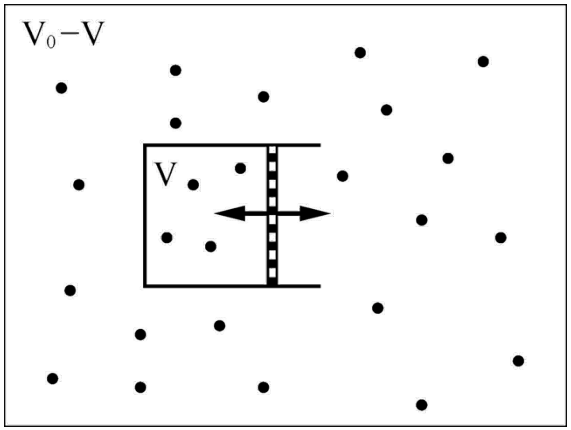


N in volume V

M in volume V_0-V

What is the statistical thermodynamics of this ensemble?

The perfect ensemble: partition function



$$Q_{NVT} = \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

$$Q_{MV_0,NV,T} = \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3M-N}\left(M-N\right)!} \int \mathrm{ds}^{M-N} \exp\left[-\beta U_0\left(\mathrm{s}^{M-N}; L\right)\right] \frac{V^N}{\Lambda^{3N} N!}$$

$$\times \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

$$Q_{MV_0,NV,T} = \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3M-N}\left(M-N\right)!} \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

$$Q_{MV_0,NV,T} = \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3M-N}\left(M-N\right)!}\frac{V^N}{\Lambda^{3N}N!}\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

To get the total partition function of this system, we have to integrate over all possible volumes:

$$Q_{MV_0,N,T} = \int \mathrm{d}V \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3M-N}\left(M-N\right)!}\frac{V^N}{\Lambda^{3N}N!}\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

Now let us take the following limits:

$$\left.\begin{array}{l} M \to \infty \\ V_0 \to \infty \end{array}\right\} \rho = \frac{M}{V} \to \text{constant}$$

As the particles are an ideal gas in the big reservoir we have:

$$\rho = \beta P$$

big reservoir acts as manostat

$$Q_{MV_0,N,T} = \int \mathrm{d}V \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3M-N}\left(M-N\right)!} \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

We have

$$\left(V_0 - V\right)^{M-N} = V_0^{M-N}\left(1 - V/V_0\right)^{M-N} \approx V_0^{M-N} \exp\left[-\left(M-N\right)V/V_0\right]$$

$$\left(V_0 - V\right)^{M-N} \approx V_0^{M-N} \exp\left[-\rho V\right] = V_0^{M-N} \exp\left[-\beta P V\right]$$

This gives:

To make the partition function dimensionless (not trivial)

$$Q_{NPT} = \frac{\beta P}{N!\Lambda^{3N}} \int \mathrm{d}V \exp\left[-\beta P V\right] V^N \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

NPT Ensemble

Partition function:

$$Q_{NPT} = \frac{\beta P}{N!\Lambda^{3N}} \int \mathrm{d}V \exp\left[-\beta PV\right] V^N \int \mathrm{d}\mathbf{s}^N \exp\left[-\beta U\left(\mathbf{s}^N; L\right)\right]$$

Probability to find a particular configuration:

$$N_{NPT}\left(V, \mathbf{s}^N\right) \propto V^N \exp[$$

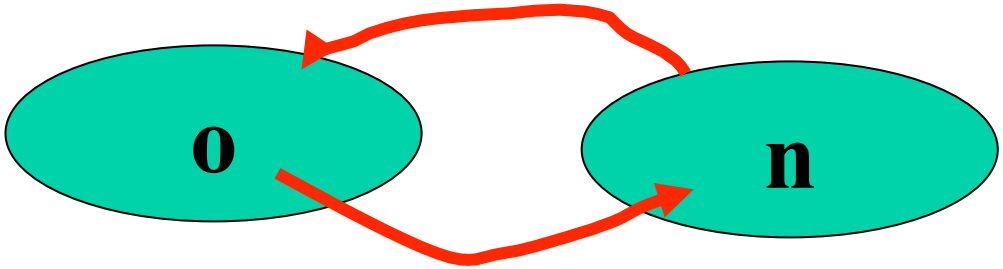
Sample a particular conf

- change of volume
- change of reduced co

Acceptance rules ??

Detailed balance

Detailed balance



$$K(o \to n) = K(n \to o)$$

$$K(o \to n) = N(o) \times \alpha(o \to n) \times \mathrm{acc}(o \to n)$$

$$K(n \to o) = N(n) \times \alpha(n \to o) \times \mathrm{acc}(n \to o)$$

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n) \times \alpha(n \to o)}{N(o) \times \alpha(o \to n)} = \frac{N(n)}{N(o)}$$

NPT-*ensemble*

$$N_{NPT}\left(V,\mathbf{s}^N\right)\propto V^N\exp\left[-\beta PV\right]\exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{N(n)}{N(o)}$$

Suppose we change the position of a randomly selected particle

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{V^N\exp\left[-\beta PV\right]\exp\left[-\beta U\left(\mathrm{s}_\mathrm{n}^\mathrm{N};L\right)\right]}{V^N\exp\left[-\beta PV\right]\exp\left[-\beta U\left(\mathrm{s}_\mathrm{o}^\mathrm{N};L\right)\right]}$$

$$=\frac{\exp\left[-\beta U\left(\mathrm{s}_\mathrm{n}^\mathrm{N};L\right)\right]}{\exp\left[-\beta U\left(\mathrm{s}_\mathrm{o}^\mathrm{N};L\right)\right]}=\exp\left\{-\beta\left[U(n)-U(o)\right]\right\}$$

NPT-*ensemble*

$$N_{NPT}\left(V,\mathbf{s}^N\right)\propto V^N\exp\left[-\beta PV\right]\exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{N(n)}{N(o)}$$

Suppose we change the ***volume*** of the system

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{V_n^{\,N}\exp\left[-\beta PV_n\right]\exp\left[-\beta U\left(\mathrm{s}^{\mathrm{N}};L_n\right)\right]}{V_o^{\,N}\exp\left[-\beta PV_o\right]\exp\left[-\beta U\left(\mathrm{s}^{\mathrm{N}};L_o\right)\right]}$$

$$=\left(\frac{V_n}{V_o}\right)^N\exp\left[-\beta P\left(V_n-V_o\right)\right]\exp\left\{-\beta\left[U\left(n\right)-U\left(0\right)\right]\right\}$$

Algorithm: NPT

- Randomly change the position of a particle
- Randomly change the volume

Algorithm 10 (Basic NPT-Ensemble Simulation)

```
 PROGRAM mc_npt                          basic NPT ensemble simulation

 do icycl=1,ncycl                        perform ncycl MC cycles
   ran=ranf()*(npart+1)+1
   if (ran.le.npart) then
     call mcmove                         perform particle displacement
   else
     call mcvol                          perform volume change
   endif
   if (mod(icycl,nsamp).eq.0)
+    call sample                         sample averages
 enddo
 end
```

Algorithm 2 (Attempt to Displace a Particle)

```
      SUBROUTINE mcmove                attempts to displace a particle

      o=int(ranf()*npart)+1            select a particle at random
      call ener(x(o),eno)              energy old configuration
      xn=x(o)+(ranf()-0.5)*delx        give particle random displacement
      call ener(xn,enn)                energy new configuration
      if (ranf().lt.exp(-beta          acceptance rule (3.2.1)
     +    *(enn-eno)) x(o)=xn          accepted: replace x(o) by xn
      return
      end
```

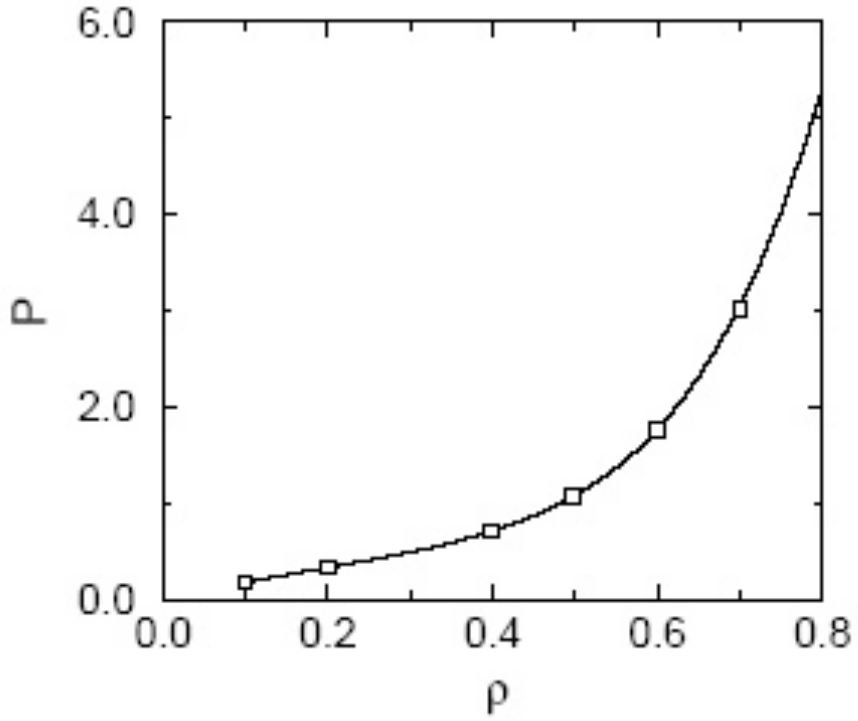
Comments to this algorithm:

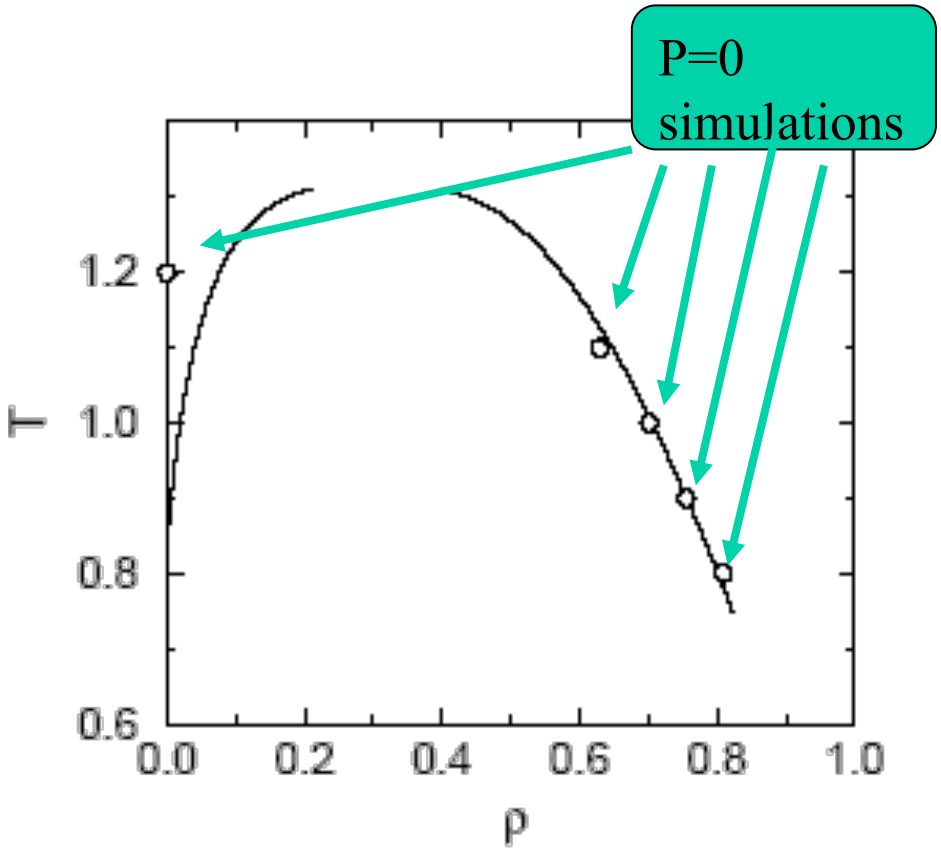
1. *Subroutine* `ener` *calculates the energy of a particle at the given position.*
2. *Note that, if a configuration is rejected, the old configuration is retained.*
3. *The* `ranf()` *is a random number uniform in* $[0, 1]$.

Algorithm 11 (Attempt to Change the Volume)

```
      SUBROUTINE mcvol                          attempts to change
                                                the volume
      call toterg(box,eno)                      total energy old conf.
      vo=box**3                                 determine old volume
      lnvn=log(vo)+(ranf()-0.5)*vmax            perform random walk in ln V
      vn=exp(lnvn)
      boxn=vn**(1/3)                            new box length
      do i=1,npart
        x(i)=x(i)*boxn/box                      rescale center of mass
      enddo
      call toterg(boxn,enn)                     total energy new conf.
      arg=-beta*((enn-eno)+p*(vn-vo)
     + -(npart+1)*log(vn/vo)/beta)              appropriate weight function!
      if (ranf().gt.exp(arg)) then              acceptance rule (5.2.3)
        do i=1,npart                            REJECTED
          x(i)=x(i)*box/boxn                    restore the old positions
        enddo
      endif
      return
      end
```

NPT simulations





Setting pressure to zero will give liquid coexistence except close to critical point: why?

Measured and Imposed Pressure

- Imposed pressure P
- Measured pressure $\langle P_V \rangle$ from virial

$$P_V = -\left(\frac{\partial F}{\partial V}\right)_{N,T}$$

$$p(V) = \frac{\exp\left[-\beta\left(F(V) + PV\right)\right]}{Q_{NPT}}$$

$$Q_{NPT} = \beta P \int dV \exp\left[-\beta\left(F(V) + PV\right)\right]$$

In fact this is βG

$$\langle P_V \rangle = -\left\langle \left(\frac{\partial F}{\partial V} \right)_{N,T} \right\rangle$$

Measured and Imposed Pressure

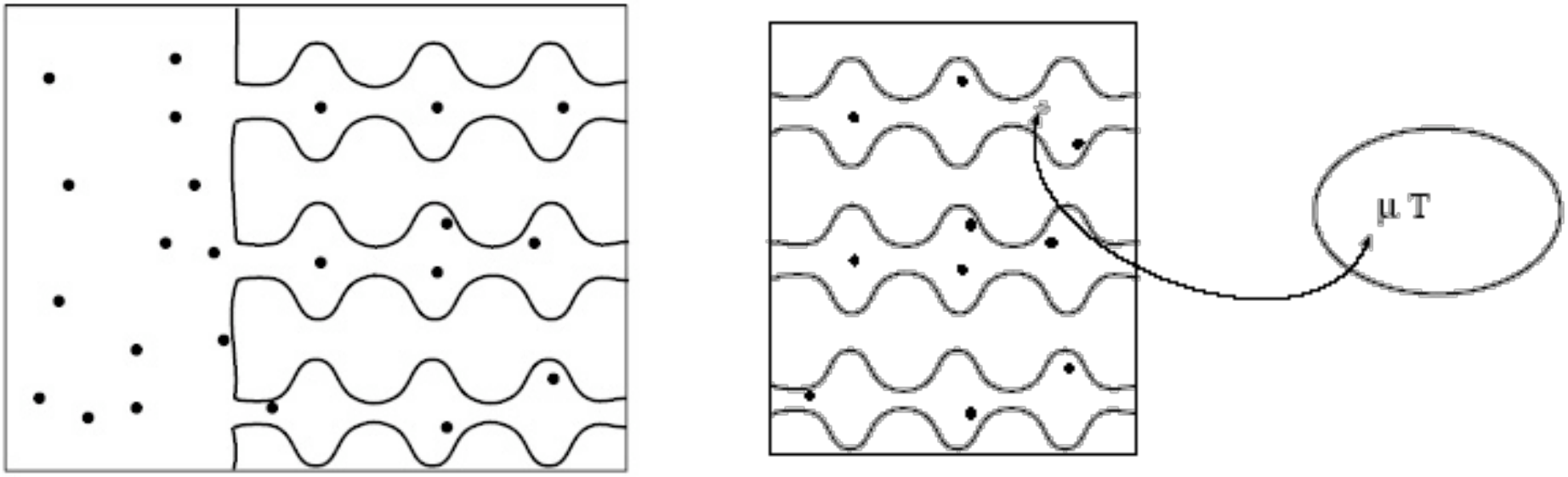
- Partial integration $\int_a^b f dg = [fg]_a^b - \int_a^b g df$
- For V=0 and V=∞ $\exp\left[-\beta\left(F(V) + PV\right)\right] = 0$
- Therefore,

$$\langle P_V \rangle = \frac{\beta P}{Q(NPT)} \int dV \frac{\exp[-\beta PV]}{\beta} \frac{\partial \exp[-\beta F(V)]}{\partial V}$$

$$\langle P_V \rangle = \frac{\beta P}{Q(NPT)} \int dVP \exp\left[-\beta\left(F(V) + PV\right)\right] = P$$

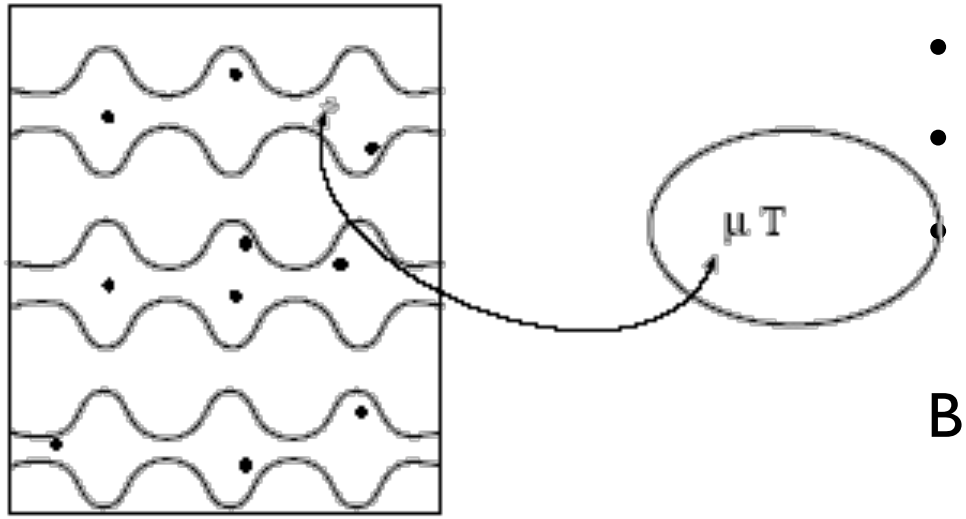
Grand-canonical ensemble

Suppose we have a gas in a porous material



What are the equilibrium conditions?

Grand-canonical ensemble

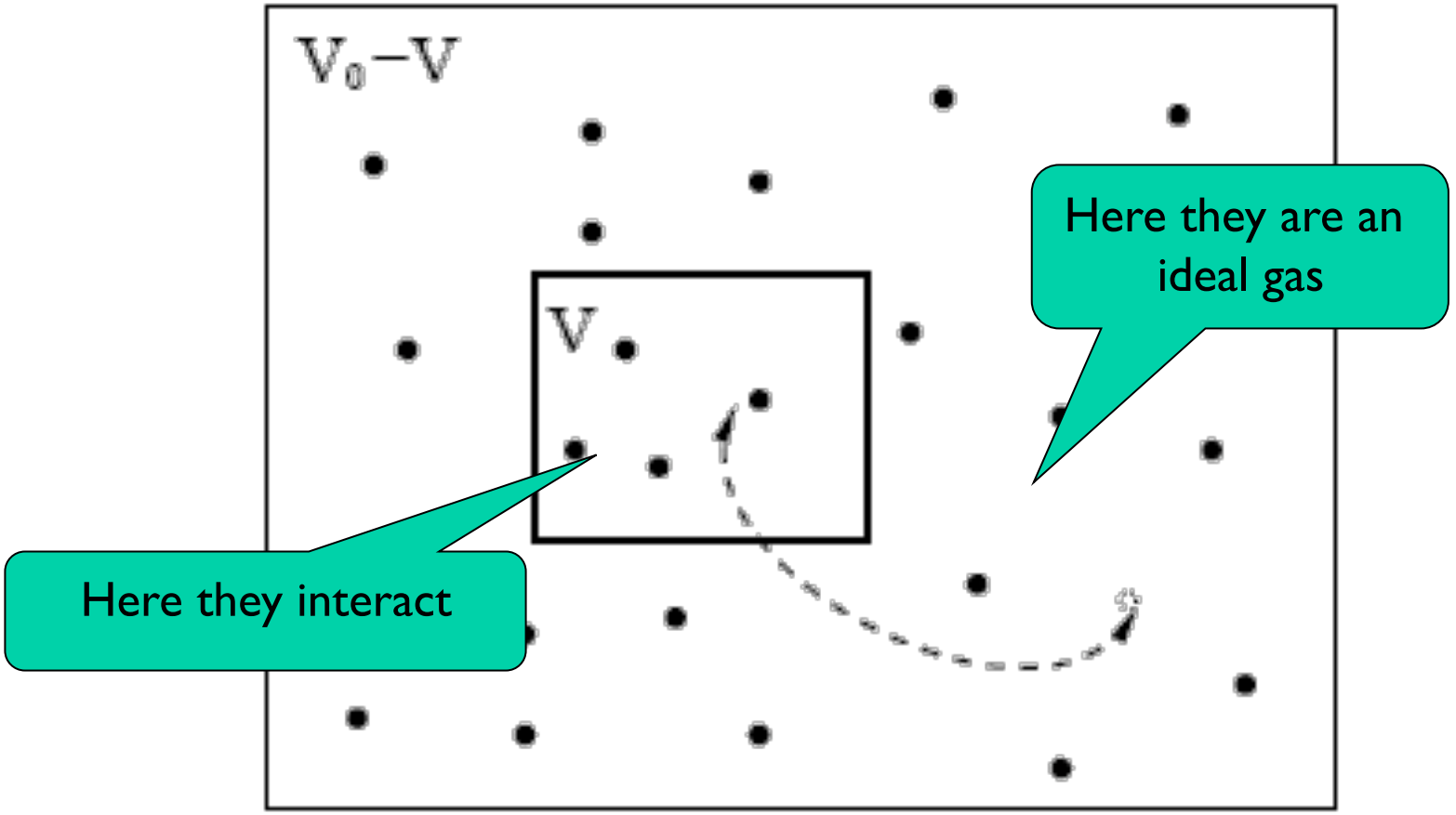


We impose:

- Temperature (T)
- Chemical potential (μ)
- Volume (V)

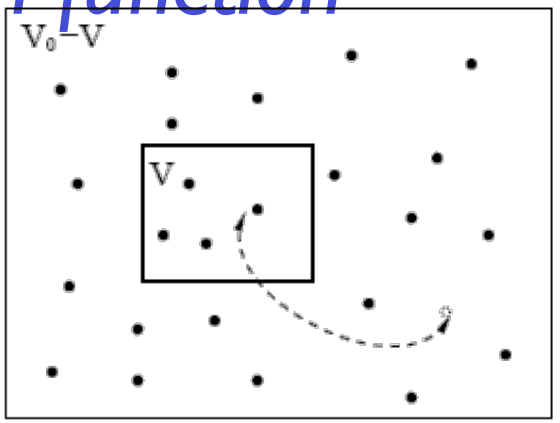
But **NOT** pressure

The μerfect ensemble



What is the statistical thermodynamics of this ensemble?

The μerfect ensemble: partition function



$$Q_{NVT} = \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

$$Q_{MV_0,NV,T} = \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3M-N}\left(M-N\right)!} \int \mathrm{ds}^{M-V} \exp\left[-\beta U_0\left(\mathrm{s}^{M-N}; L\right)\right] \frac{V^N}{\Lambda^{3N} N!}$$

$$\times \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

$$Q_{MV_0,NV,T} = \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3M-N}\left(M-N\right)!} \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

$$Q_{MV_0,NV,T} = \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3M-N}\left(M-N\right)!}\frac{V^N}{\Lambda^{3N}N!}\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

To get the total partition function of this system, we have to sum over all possible numbers of particles N

$$Q_{MV_0,N,T} = \sum_{N=0}^{N=M} \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3M-N}\left(M-N\right)!}\frac{V^N}{\Lambda^{3N}N!}\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

Now let us take the limits:

$$\left.\begin{array}{l} M \to \infty \\ V_0 \to \infty \end{array}\right\} \rho = \frac{M}{V} \to \text{constant}$$

As the particles are an ideal gas in the big reservoir we have:

$$\mu = k_B T \ln\left(\Lambda^3 \rho\right)$$

$$Q_{\mu VT} = \sum_{N=0}^{N=\infty} \frac{\exp\left(\beta\mu N\right)V^N}{\Lambda^{3N}N!}\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

μVT Ensemble

Partition function:

$$Q_{\mu VT} = \sum_{N=0}^{N=\infty} \frac{\exp(\beta\mu N) V^N}{\Lambda^{3N} N!} \int ds^N \exp\left[-\beta U\left(s^N; L\right)\right]$$

Probability to find a particular configuration:

$$N_{\mu VT}\left(V, \mathbf{s}^N\right) \propto \frac{\exp(\beta\mu N) V^N}{\Lambda^{3N} N!} \exp\left[-\beta U\left(s^N; L\right)\right]$$

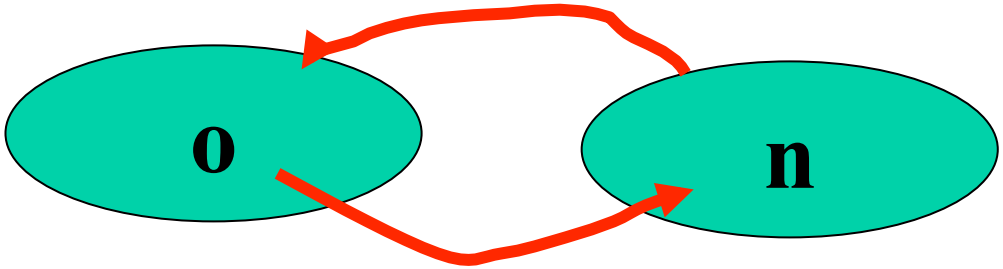
Sample a particular co

- Change of the nu
- Change of reduced

Acceptance rules ??

Detailed balance

Detailed balance



$$K(o \to n) = K(n \to o)$$

$$K(o \to n) = N(o) \times \alpha(o \to n) \times \mathrm{acc}(o \to n)$$

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$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{N(n) \times \alpha(n \to o)}{N(o) \times \alpha(o \to n)} = \frac{N(n)}{N(o)}$$

μVT-ensemble

$$N_{\mu VT}\left(V,\mathbf{s}^N\right)\propto\frac{\exp\left(\beta\mu N\right)V^N}{\Lambda^{3N}N!}\exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{N(n)}{N(o)}$$

Suppose we change the position of a randomly selected particle

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{\cancel{\frac{\exp\left(\beta\mu N\right)V^N}{\Lambda^{3N}N!}}\exp\left[-\beta U\left(\mathrm{s}_\mathrm{n}^\mathrm{N};L\right)\right]}{\cancel{\frac{\exp\left(\beta\mu N\right)V^N}{\Lambda^{3N}N!}}\exp\left[-\beta U\left(\mathrm{s}_\mathrm{o}^\mathrm{N};L\right)\right]}$$

$$=\exp\left\{-\beta\left[U\left(n\right)-U\left(0\right)\right]\right\}$$

μVT-*ensemble*

$$N_{\mu VT}\left(V,\mathbf{s}^N\right)\propto\frac{\exp\left(\beta\mu N\right)V^N}{\Lambda^{3N}N!}\exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{N(n)}{N(o)}$$

Suppose we change the ***number of particles*** of the system

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{\dfrac{\exp\left(\beta\mu\left(N+1\right)\right)V^{N+1}}{\Lambda^{3N+3}\left(N+1\right)!}\exp\left[-\beta U\left(\mathrm{s}^{\mathrm{N+1}};L_n\right)\right]}{\dfrac{\exp\left(\beta\mu N\right)V^N}{\Lambda^{3N}N!}\exp\left[-\beta U\left(\mathrm{s}^{\mathrm{N}};L_o\right)\right]}$$

$$=\frac{\exp\left(\beta\mu\right)V}{\Lambda^3\left(N+1\right)}\exp\left[-\beta\Delta U\right]$$

Algorithm 12 (Basic Grand-Canonical Ensemble Simulation)

```
 PROGRAM mc_gc                          basic μVT ensemble
                                        simulation
 do icycl=1,ncycl                       perform ncycl MC cycles
  ran=int(ranf()*(npav+nexc))+1
  if (ran.le.npart) then
    call mcmove                         displace a particle
  else
    call mcexc                          exchange a particle
  endif                                 with the reservoir
  if (mod(icycl,nsamp).eq.0)
+   call sample                         sample averages
 enddo
 end
```

Comments to this algorithm:

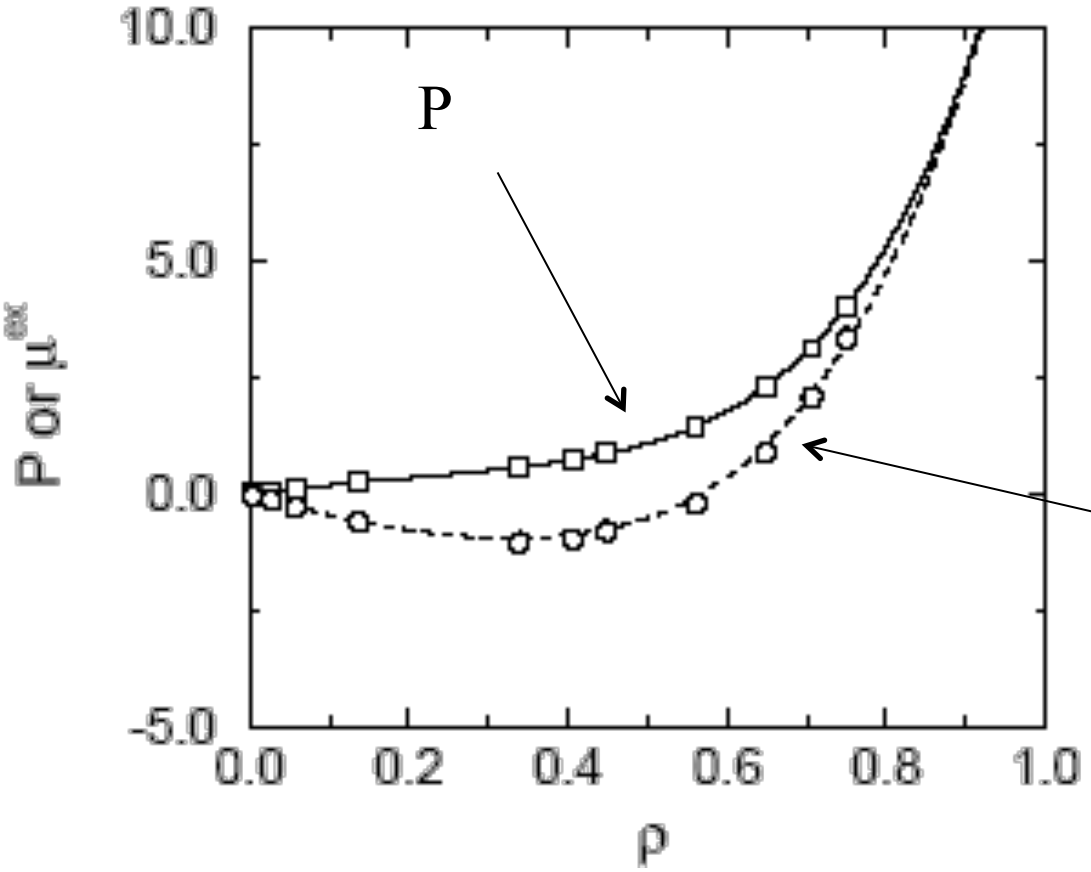
1. *This algorithm ensures that, after each MC step, detailed balance is obeyed. Per cycle we perform on average* `npav` *attempts*[6] *to displace particles and* `nexc` *attempts to exchange particles with the reservoir.*
2. *Subroutine* `mcmove` *attempts to displace a particle (Algorithm 2), subroutine* `mcexc` *attempts to exchange a particle with a reservoir (Algorithm 13), and subroutine* `sample` *samples quantities every* `nsamp` *cycle.*

Algorithm 13 (Attempt to Exchange a Particle with a Reservoir)

```
 SUBROUTINE mcexc                    attempt to exchange a particle
                                     with a reservoir
 if (ranf().lt.0.5) then             decide to remove or add a particle
   if (npart.eq.0) return            test whether there is a particle
   o=int(npart*ranf())+1             select a particle to be removed
   call ener(x(o),eno)               energy particle o
   arg=npart*exp(beta*eno)           acceptance rule (5.6.9)
+       /(zz*vol)
   if (ranf().lt.arg) then
     x(o)=x(npart)                   accepted: remove particle o
     npart=npart-1
   endif
 else
   xn=ranf()*box                     new particle at a random position
   call ener(xn,enn)                 energy new particle
   arg=zz*vol*exp(-beta*enn)         acceptance rule (5.6.8)
+       /(npart+1)
   if (ranf().lt.arg) then
     x(npart+1)=xn                   accepted: add new particle
     npart=npart+1
   endif
 endif
 return
 end
```

Comment to this algorithm:

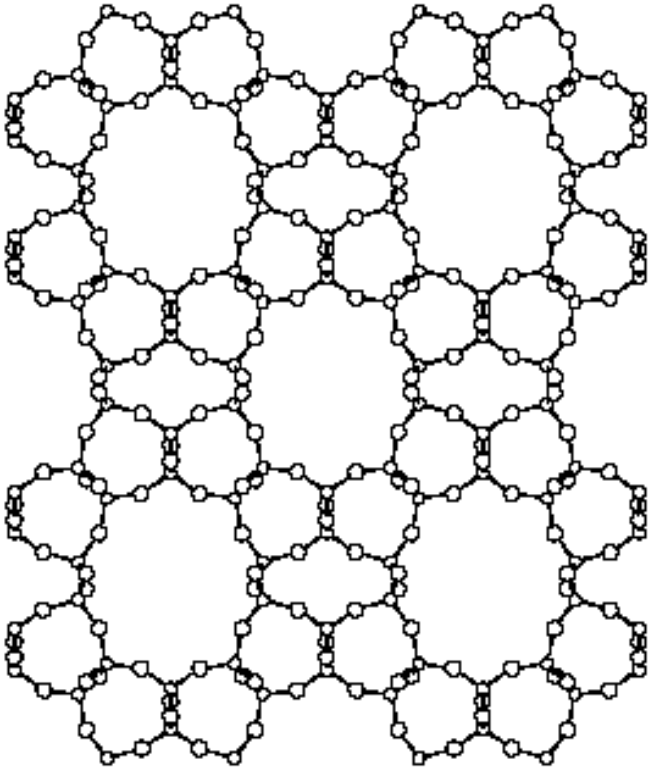
Application: equation of state of Lennard-Jones at T=2.0

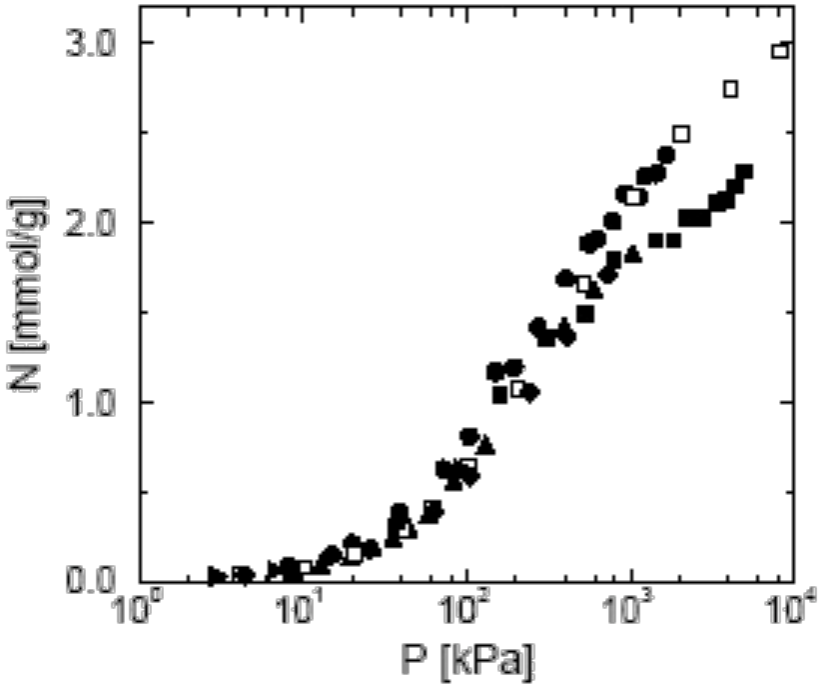


$$\mu = kT \ln \Lambda^3 \rho + \mu^{ex}$$

Potential problem: at high densities acceptance goes down.

Application: adsorption in zeolites





Semi grand ensemble

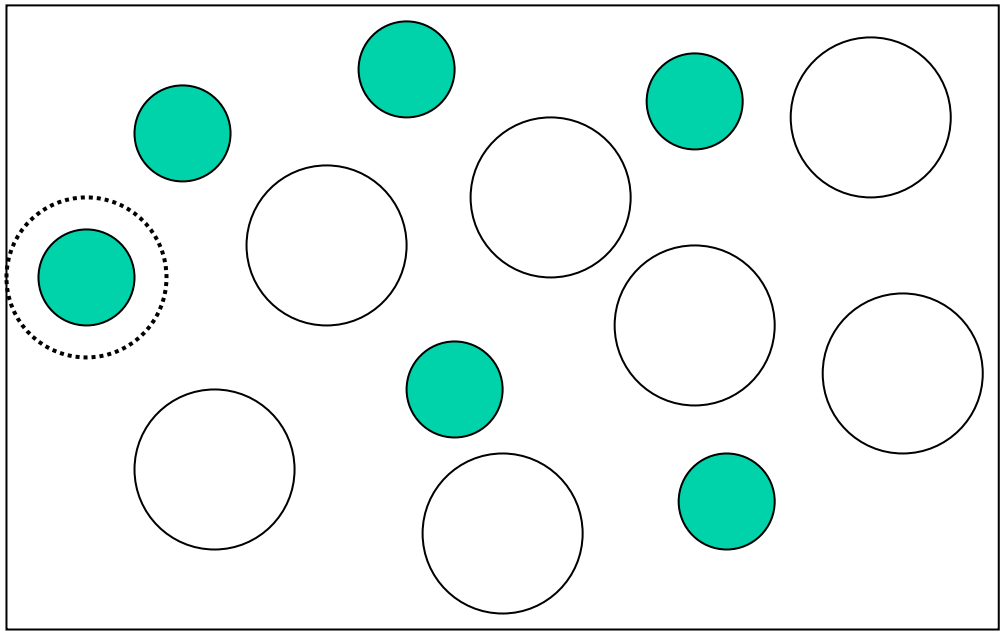
- For mixtures an additional ensemble exists: semigrand
- Constant $N\Delta\mu T$:
  - The difference between the chemical potentials of the components is fixed
  - total number of particles is fixed

- For a binary mixture
  - N_1, N_2 are allowed to change, but $N_1+N_2=N$
  - μ_2, μ_1 are allowed to change, but $\Delta\mu = \mu_2 - \mu_1$

$$\Xi = \frac{\beta P}{N!\Lambda^{3N}} \int dV V^N \exp[-\beta PV] \times \sum_{identities} \exp[\beta N_2 \Delta\mu] \times \int ds^N \exp[-\beta U(s^N)]$$

In binary mixture just 1,2

MC move changes identity



$$P_{acc}(1 \rightarrow 2) = \min[1, \exp[-\beta U + \beta \Delta \mu]$$

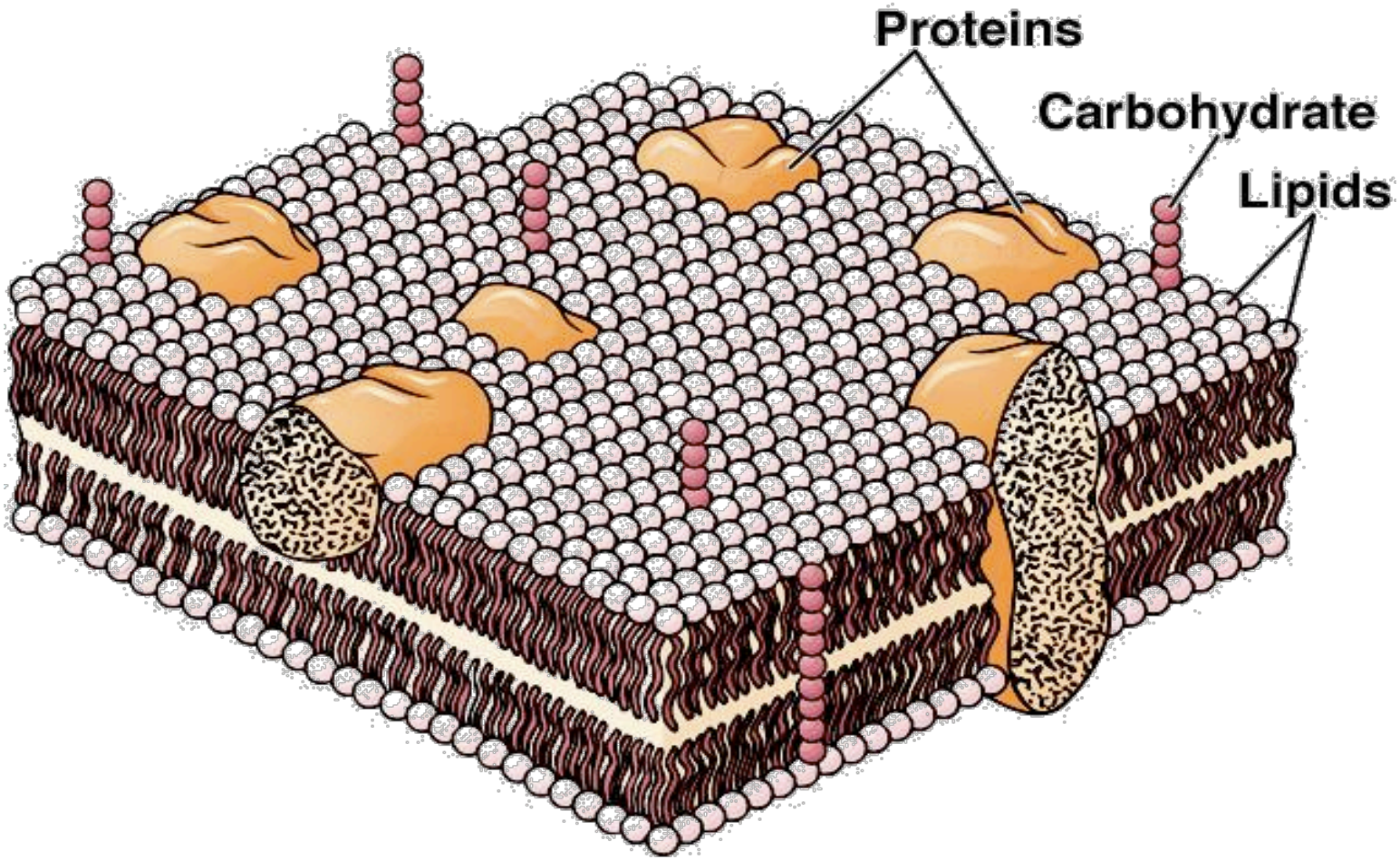
Advantage: at high densities still good acceptance

Summary

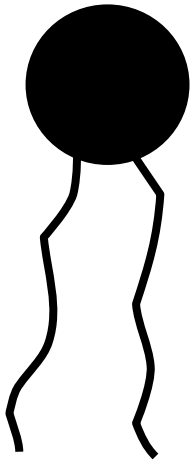
Ensemble	Constant (Imposed)	Fluctuating (Measured)	Function
NVT	N,V,T	P	$\beta F=-\ln Q(N,V,T)$
NPT	N,P,T	V	$\beta G=-\ln Q(N,P,T)=\beta F+\beta PV$
μVT	μ,V,T	N	$\beta\Omega=-\ln Q(\mu,V,T)=-\beta PV$
$\Delta\mu VT$	$\Delta\mu VT$	μ_i ,N_i	$\beta Y=-\ln\Xi(\Delta\mu,V,T)$

Exotic ensembles

What to do with a biological membrane?

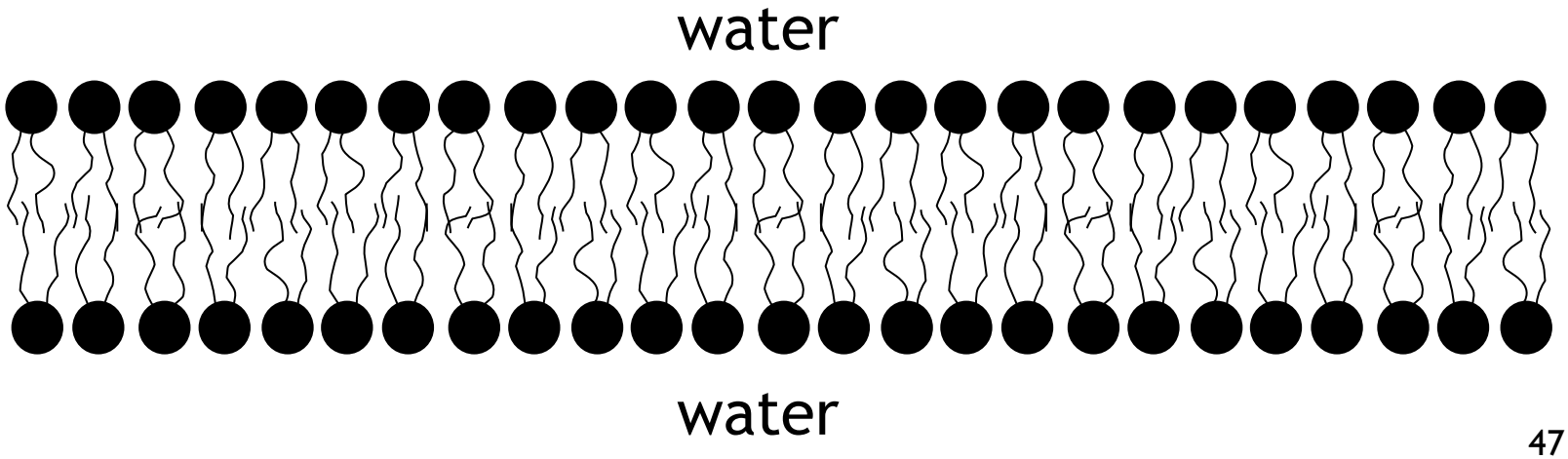


Model membrane: Lipid bilayer

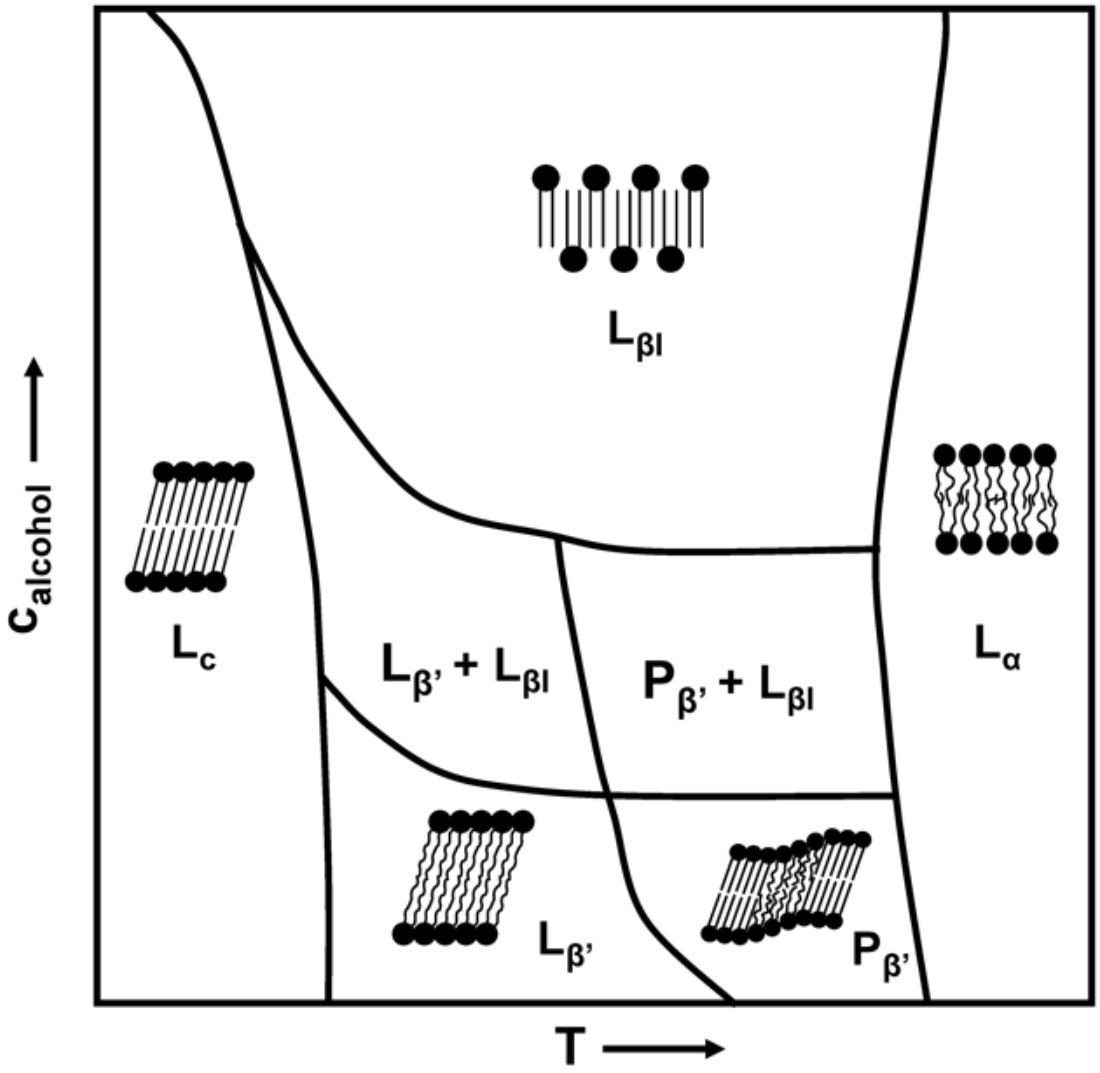


hydrophilic head group

two hydrophobic tails



Phase diagram: lipid-alcohol mixture

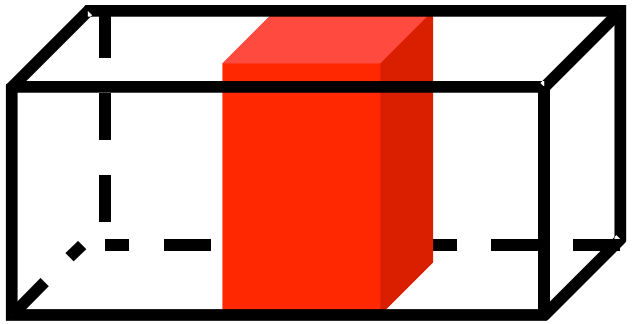


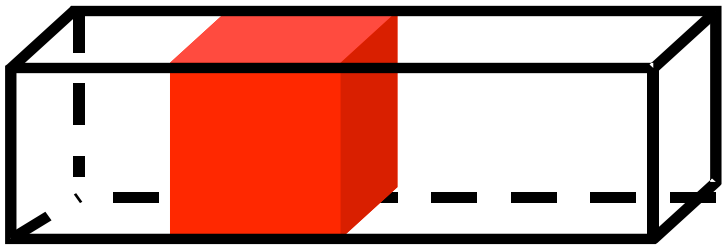
Surface Tension γ controls area per lipid

$\gamma<0$	compressed bilayer
$\gamma=0$	tensionless bilayer
$\gamma>0$	stretched bilayer

Simulations at imposed surface tension

- Simulation to a constant surface tension
  - Simulation box: allow the area of the bilayer to change in such a way that the volume is constant.





Constant surface tension simulation

$$N_{N\gamma T}\left(A,\mathbf{r}^N\right) \propto \exp[-\beta(\mathrm{U}(\mathbf{r}^N)-\gamma\,\mathrm{A})]$$

A ➡ A’

L ➡ L’

A L = A’ L’ = V

$$P_{acc} = \min(1,\exp\{-\beta[\mathrm{U}(\mathbf{s}^N;\mathrm{A}')-\mathrm{U}(\mathbf{s}^N;\mathrm{A})-\gamma(\mathrm{A}'-\mathrm{A})]\})$$

Tensionless state: $\gamma = 0$

$\gamma(A_o)$ = -0.3 +/- 0.6

$\gamma(A_o)$ = 2.5 +/- 0.3

$\gamma(A_o)$ = 2.9 +/- 0.3