Monte Carlo Methods

Ensembles (Chapter 5)
Biased Sampling (Chapter 14)
Practical Aspects

Classical and Statistical Thermodynamics

Problem: we have a set of coordinates and velocities -what to do with it?

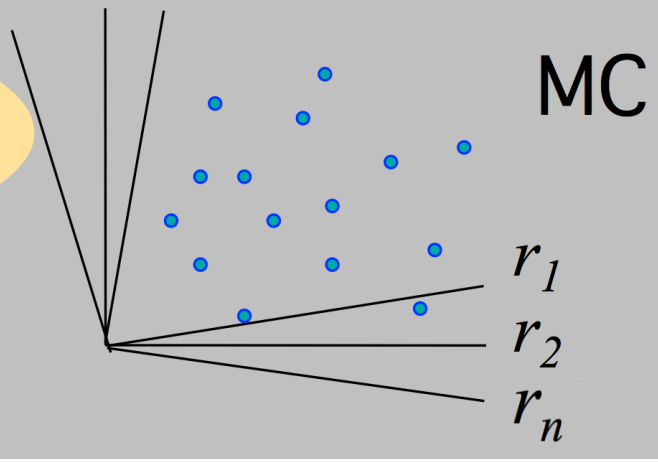
- Statistical Thermodynamics
  - The probability to find a particular configuration
  - Properties are expressed in term of averages
  - Free energies
- Thermodynamics: relation of the free energies to thermodynamic properties

Monte Carlo

What is the correct probability?
Statistical Thermodynamics

- Generate a set of configurations with the *correct* probability
- Compute the thermodynamic and transport properties as averages over all configurations

How to compute these properties from a simulation?

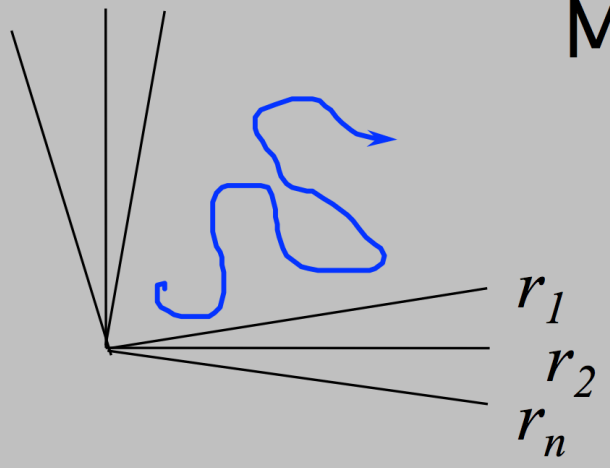


Molecular Dynamics

MD

- Theory:

$$\mathbf{F} = m\frac{d^2\mathbf{r}}{dt^2}$$



- Compute the forces on the particles
- Solve the equations of motion
- Sample after some timesteps

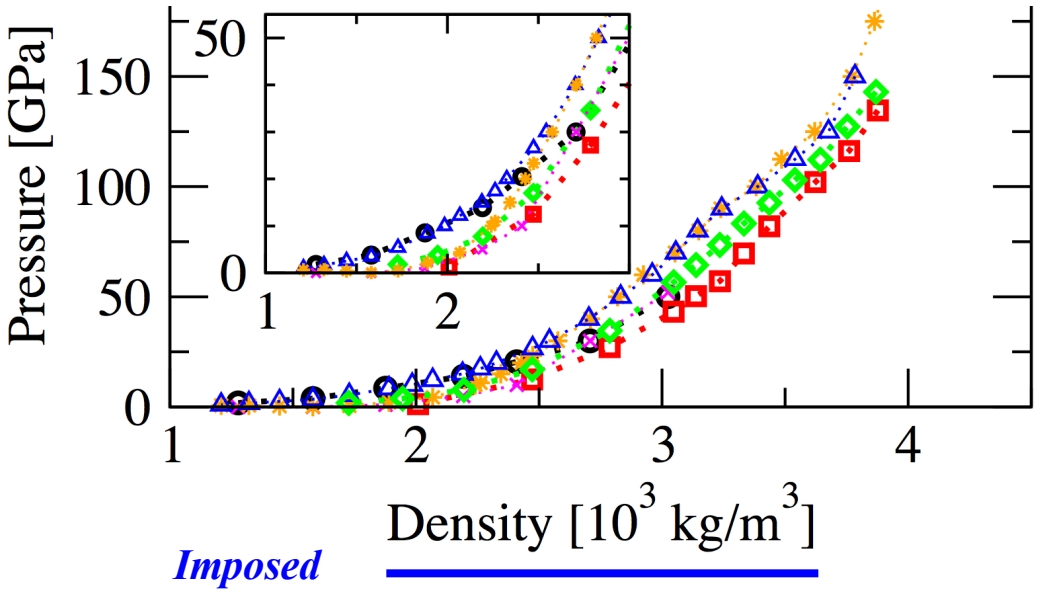
Different Ensembles

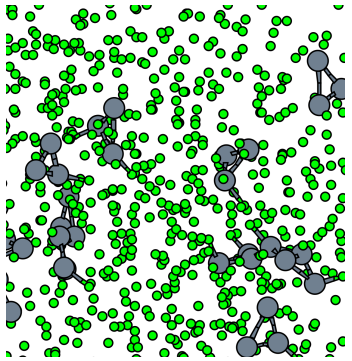
Ensemble	Name	Constant (Imposed)	Fluctuating (Measured)
NVT	Canonical	N,V,T	P
NPT	Isobaric-isothermal	N,P,T	V
μVT	Grand-canonical	μ,V,T	N

NVT

Liquids

Equation of State of Liquid Carbon





Imposed

… if force is difficult to calculate …
e.g. carbon force field

TABLE I. Parameters of the LCBOPII. The units of energy and length are eV and Å, respectively.

Switch	q	q_{min}	q_{max}	p	Switch	q	q_{min}	q_{max}	p	Switch	q	q_{min}	q_{max}	p
S_{sr}^{down}	r_{ij}	1.7	2.2	3.0	S_{mr}^{up}	r_{ij}	1.7	2.2	−2.0	S_{N}^{down}	r_{ij}	1.7	2.2	−3.0
S_{lr}^{down}	r_{ij}	5.5	6.0	0	S_{M}^{up}	N_{ki}	2.0	3.0	0	S_{sat}^{down}	N_{ki}	3.0	4.0	0
S_{db}^{down}	x_{ij}^{db}	0.0	1.0	0	$S_{\gamma,0}^{up}$	γ_{ij}	0.34	0.93	0	$S_{\gamma,2}^{up}$	γ_{ij}	0.30	0.93	0

Short-range potential V^{sr}

V_R $A^{sr}=53026.92614$ $\alpha=6.74750993$

V_A $B_1^{sr}=27618.35706$ $\beta_1=6.34503890$ $B_2^{sr}=34.07142502$ $\beta_2=1.19712839$

G $g_{min}=0.0020588719$ $g_{gr}=0.0831047003$ $g_{max}=16.0$

$g_{1,0}=0.7233666272$ $g_{1,1}=1.7334665088$ $g_{1,2}=1.8701997632$

$g_{2,0}=0.73994527795$ $g_{2,1}=-1.999211817$ $g_{2,2}=-17.43251545$

$g_{2,3}=-33.96127110$ $g_{2,4}=-44.65392079$

$g_{3,0}=-15.19$ $g_{3,1}=-25.6168552398$ $g_{3,2}=-21.51728397$

$g_{3,3}=0.9899080993$ $g_{3,4}=13.66416160$

$A_{y_0}=-0.4$ $B_{y_0}=0.01875$

$A_g=5.6304664723$ $B_g=0.1516943990$ $C_g=0.009832975891$

$D_g=-0.189175977654$ $E_g=0.050977653631$

H $d=0.14$ $C_1=3.335$ $C_4=220.0$ For C_6, L, κ, R_0 and R_1 see text.

F_{ij}^{conj}

$F_{ij,0}^{conj}$

0.0000	0.0207	−0.0046	−0.1278	0.0000	0.0584	0.0416	−0.1278
0.0207	0.0000	−0.0365	−0.1043	0.0584	0.1379	0.0062	−0.1243
−0.0046	−0.0365	0.0000	−0.0273	0.0416	0.0062	0.0936	−0.0393
−0.1278	−0.1043	−0.0273	0.0000	−0.1278	−0.1243	−0.0393	0.0000

$F_{ij,1}^{conj}$

A_{ij} $\alpha_0=0.95$

T_{ij} $A_t=-13.152909887$

$B_{t1}=-0.0486839616$ $B_{t2}=3.8$ $B_{t3}=0.62$ $B_{t4}=0.005$

Long-range potential V^{lr}

$\tau_0=3.715735$ $\epsilon_1=0.002827918$ $\lambda_1=1.338162$ $\lambda_2=2.260479$ For ϵ_1, v_1, and v_2 see text.

Middle-range potential V^{mr}

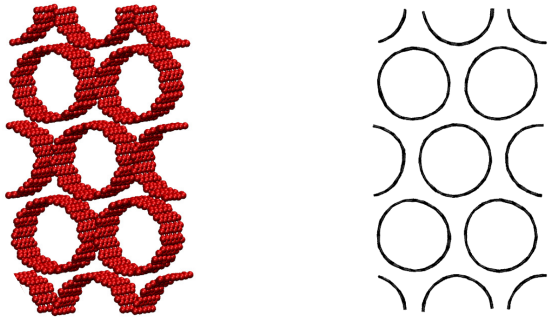
$r_1^{mr}=4.0$ $r_2^{mr}=2.9$ $A_0^{mr}=-0.2345$ $A_1^{mr}=-0.67$ $A_2^{mr}=-4.94$

Imp

NPT

Non-Isotropic Systems
e.g. Solids

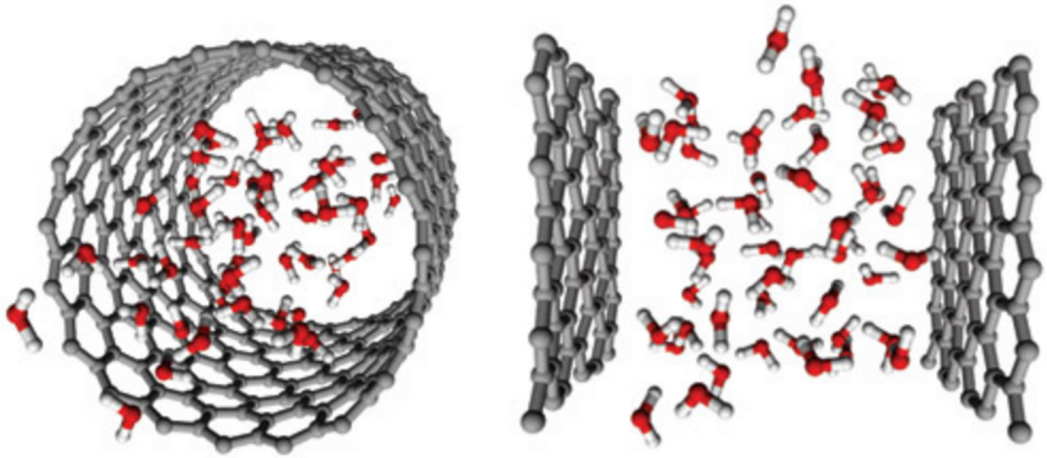
Structure and Transformation of
Carbon Nanotube Arrays



μVT

Adsorption

Adsorption in Carbon Nanostructues



Schwegler et al.

Statistical Thermodynamics

Partition function

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

Ensemble average

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

Probability to find a particular configuration

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

Free energy

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

Ensemble average

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

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

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

Generate configuration using MC:

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

Weighted Distribution

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

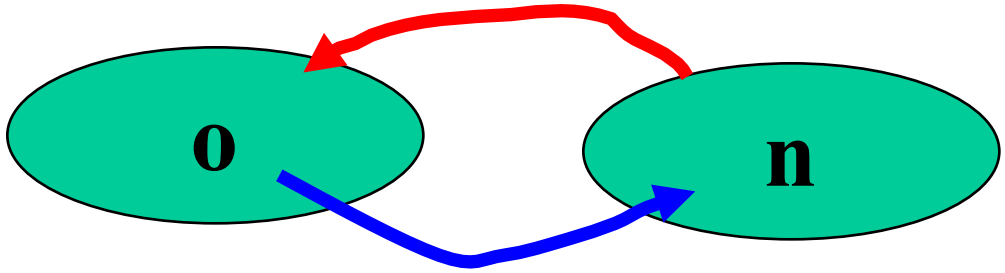
with

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

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

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

Monte Carlo: Detailed balance



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

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

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

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

- *N(o)* : total number of systems in our ensemble in state o
- *α(o → n)*: a priori probability to generate a move *o → n*
- *acc(o → n)*: probability to accept the move *o → n*

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

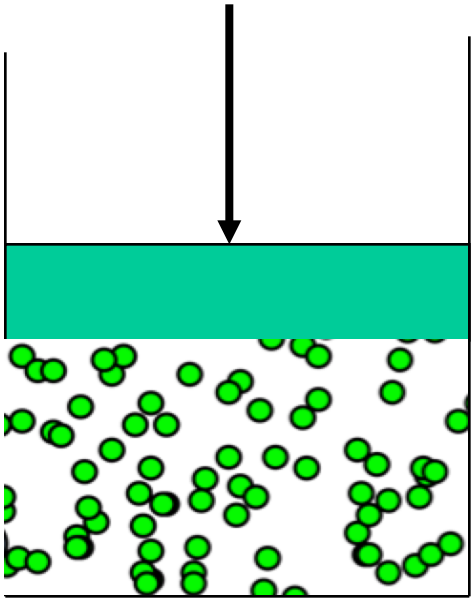
NVT-ensemble

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

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

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

NPT ensemble



We control the

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

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

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

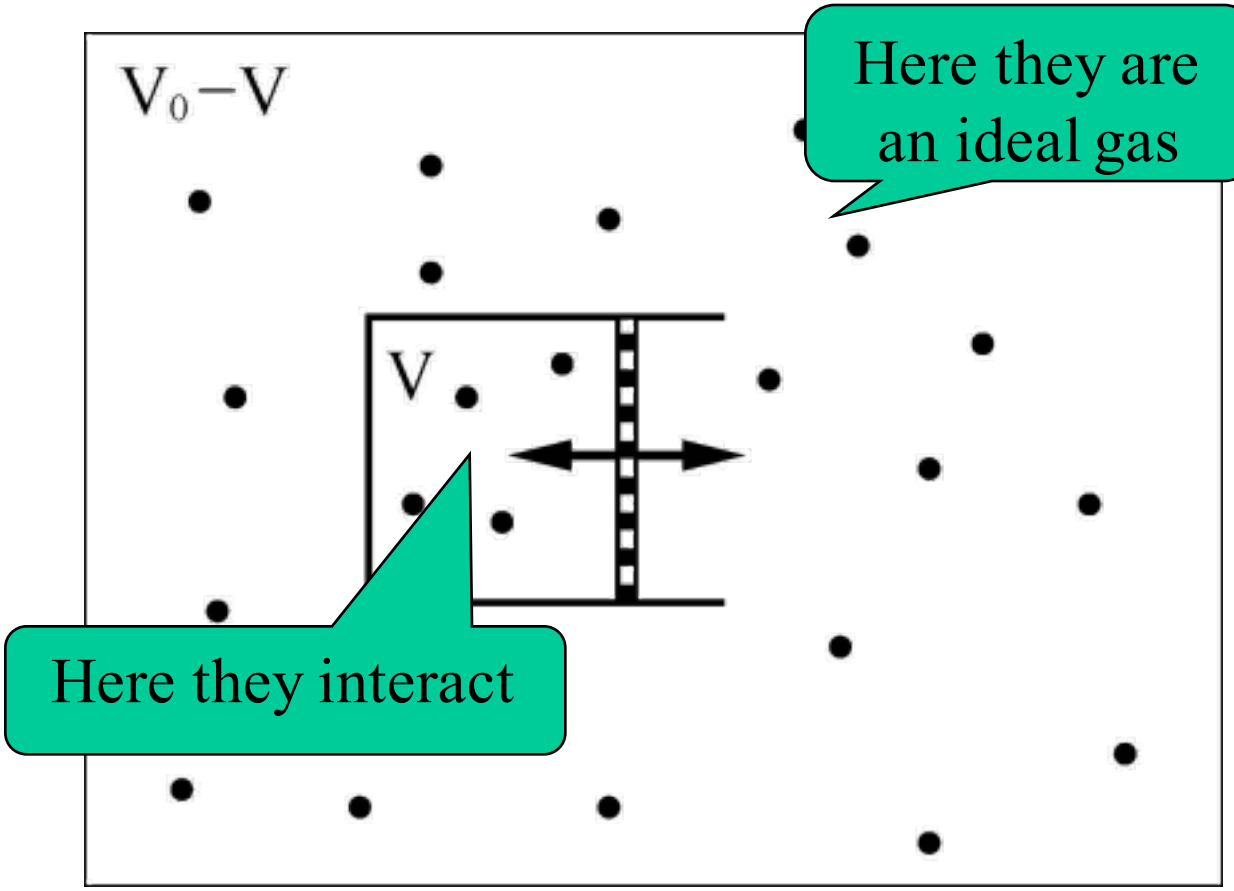
This gives for the partition function

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

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

The energy depends on the real coordinates

The NPT ensemble



V_0 : total volume
M : total number of particles

N in volume V

M-N in volume V_0-V

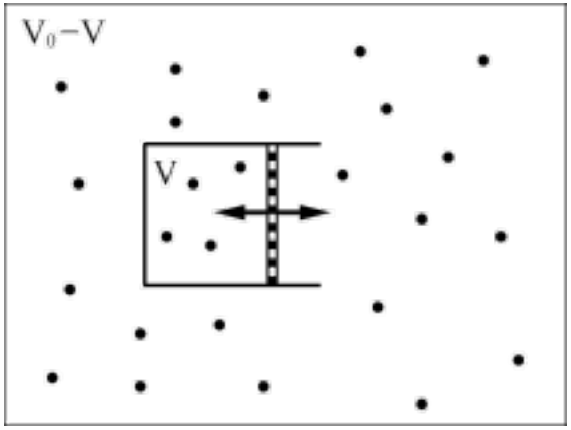
V_0 is fixed

V varies from 0 to V_0

What is the statistical thermodynamics of this ensemble?

The NPT ensemble: partition function

Fixed V



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

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

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

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

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

To get the Partition Function of this system, we have to integrate over all possible volumes:

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

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:

$$\rho = \beta P$$

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

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 (see Frenkel/Smit for more info)

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

NPT Ensemble

Partition function:

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

Probability to find a particular configuration:

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

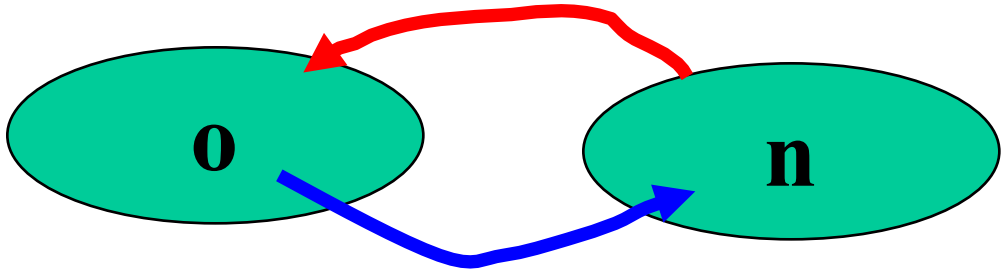
Sample a particular c

- change of volum
- change of reduced

Acceptance rules ??

Detailed balance

Detailed balance



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

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

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

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

NPT-ensemble

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

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

Suppose we change the position of a randomly selected particle

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

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

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:

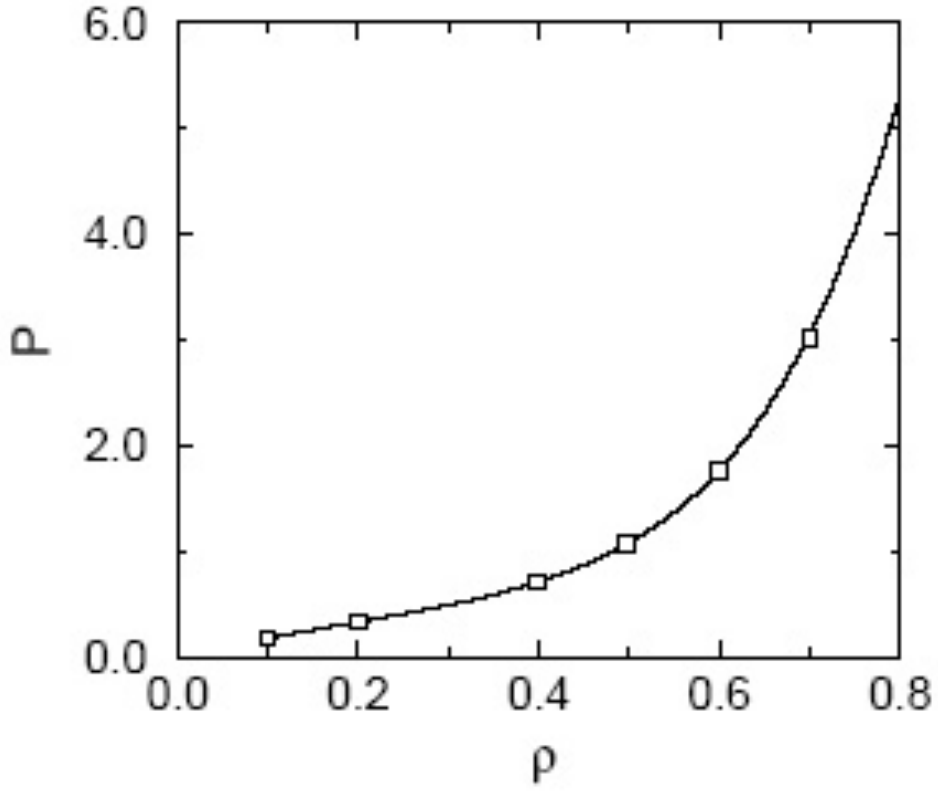
1. *Subroutine* `ener` *calculates the energy of a particle at the given position.*
2. *Note that, if a configuration is rejected, the old configuration is retained.*
3. *The* `ranf()` *is a random number uniform in* $[0, 1]$.

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

Equation of State of Lennard Jones System



Measured and Imposed Pressure

- Imposed pressure P
- Measured pressure <P> from virial

$$\langle P \rangle = -\left\langle \left(\frac{\partial F}{\partial V} \right) \right\rangle_{N,T} = \frac{-\int dV V^N e^{-\beta PV} \int ds^N e^{-\beta U(s^N)} \left(\frac{\partial F}{\partial V} \right)_{N,T}}{\int dV V^N e^{-\beta PV} \int ds^N e^{-\beta U(s^N)}}$$

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

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

$$\langle P \rangle = - < \left(\frac{\partial F}{\partial V} \right) >_{N,T} = \frac{-\int dV V^N e^{-\beta PV} \int ds^N e^{-\beta U(s^N)} \left(\frac{\partial F}{\partial V} \right)_{N,T}}{\int dV V^N e^{-\beta PV} \int ds^N e^{-\beta U(s^N)}}$$

$$\langle P \rangle = -\frac{\beta P}{Q(NPT)} \int dV \left(\frac{\partial F}{\partial V} \right)_{N,T} \exp\left[-\beta \left(F(V) + PV \right) \right]$$

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

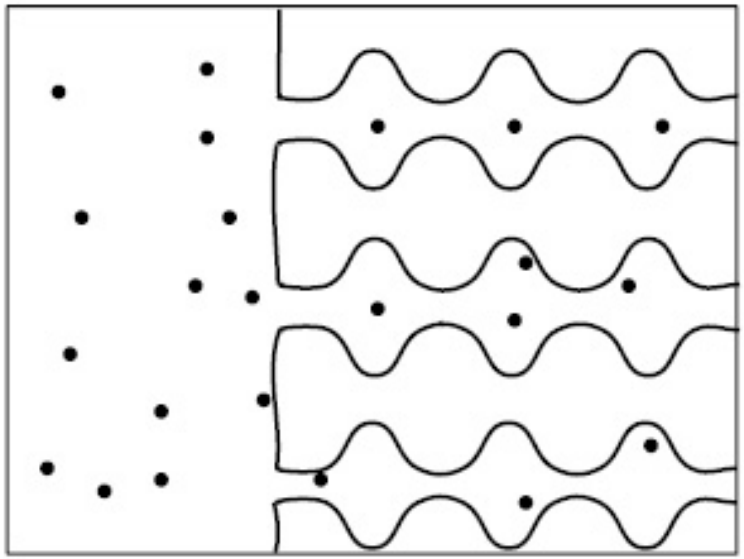
Measured and Imposed Pressure

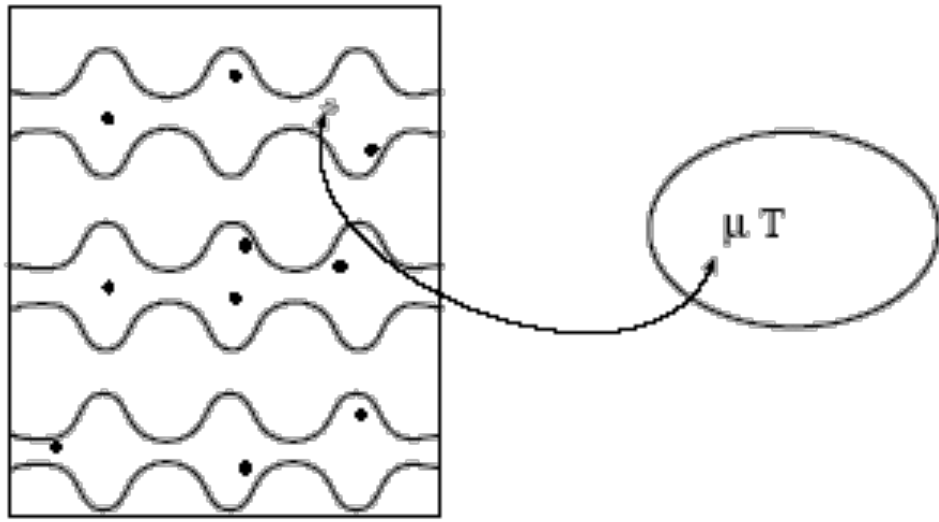
- Partial integration $\int_a^b f dg = \left[fg \right]_a^b - \int_a^b g df$
- For V=0 and V=∞ $\exp\left[-\beta \left(F\left(V\right) + PV \right) \right] = 0$
- Therefore,

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

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

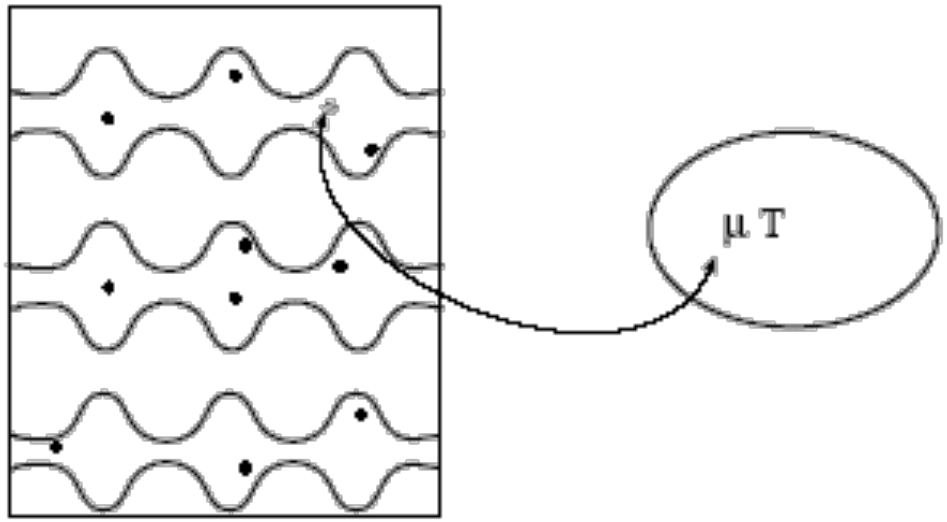
Grand-canonical ensemble





What are the equilibrium conditions?

Grand-canonical ensemble

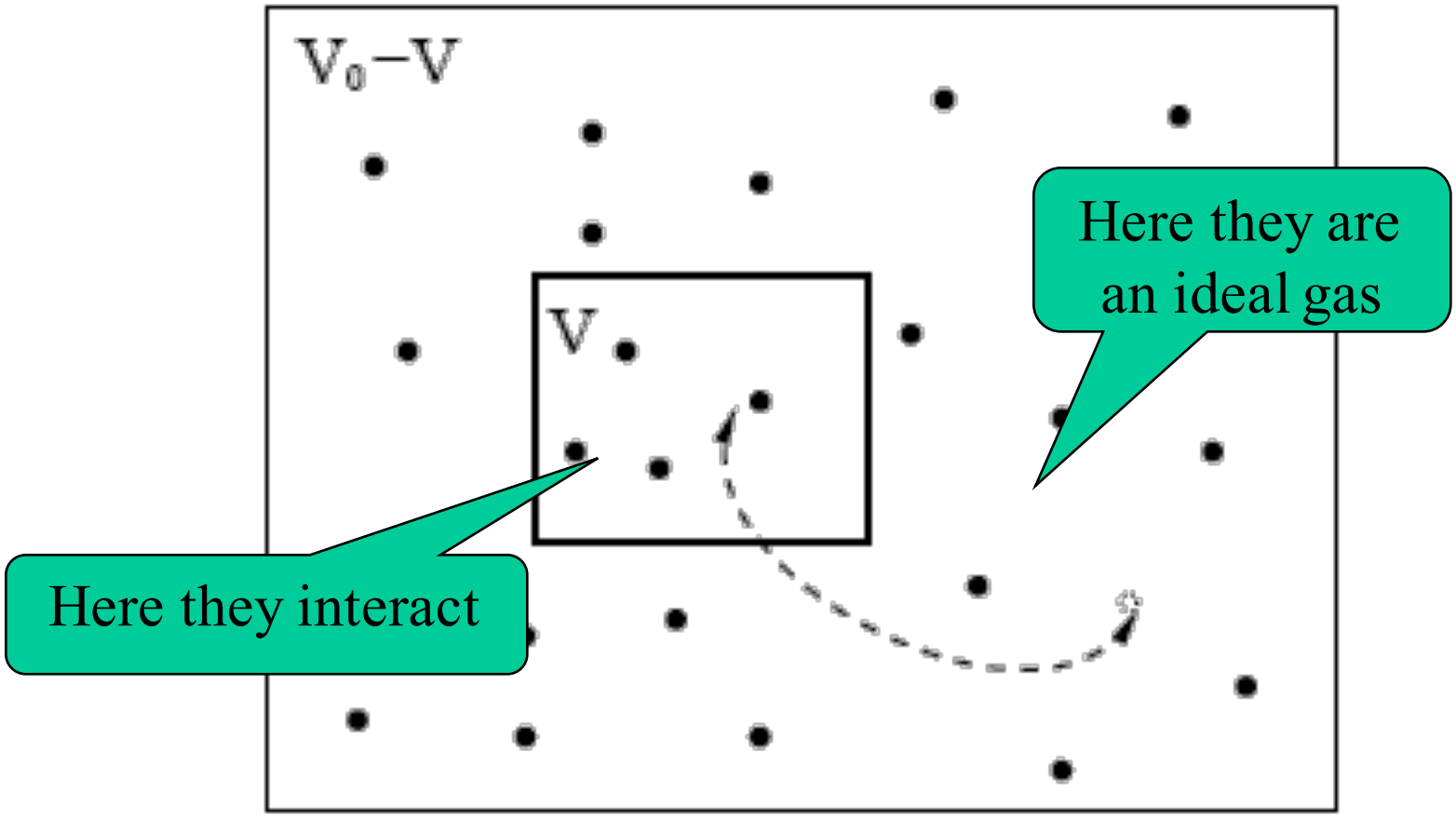


We impose:

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

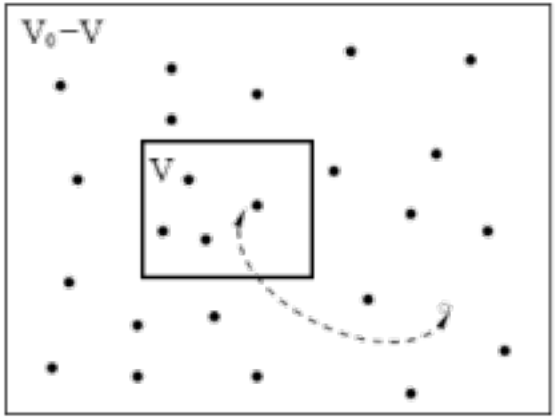
- But **NOT** pressure

The ensemble of the total system



What is the statistical thermodynamics of this ensemble?

The ensemble: partition function



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

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

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

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

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

To get the Partition Function of this system, we have to sum over all possible number of particles

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

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:

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

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

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:

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

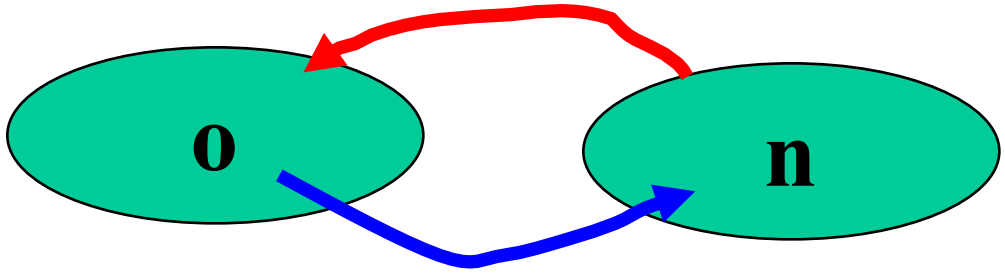
Sample a particular c

- Change of the nu
- Change of reduce

Acceptance rules ??

Detailed balance

Detailed balance



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

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

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

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

μVT-ensemble

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

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

Suppose we change the position of a randomly selected particle

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

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

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

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

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

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
```

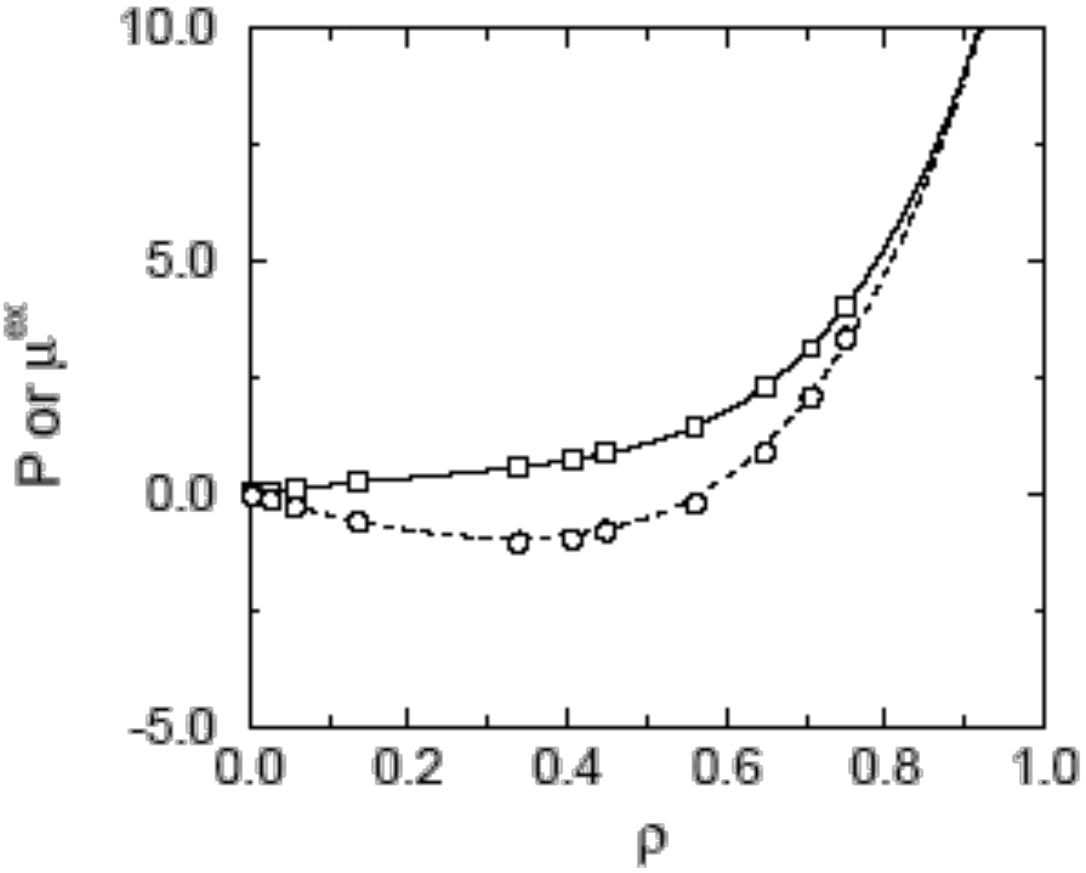
Comments to this algorithm:

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.*

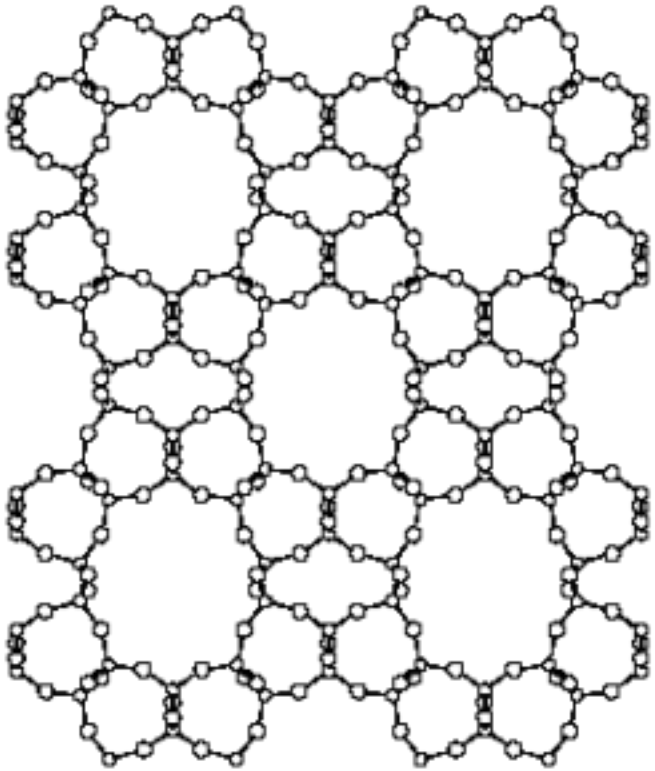
Algorithm 13 (Attempt to Exchange a Particle with a Reservoir)

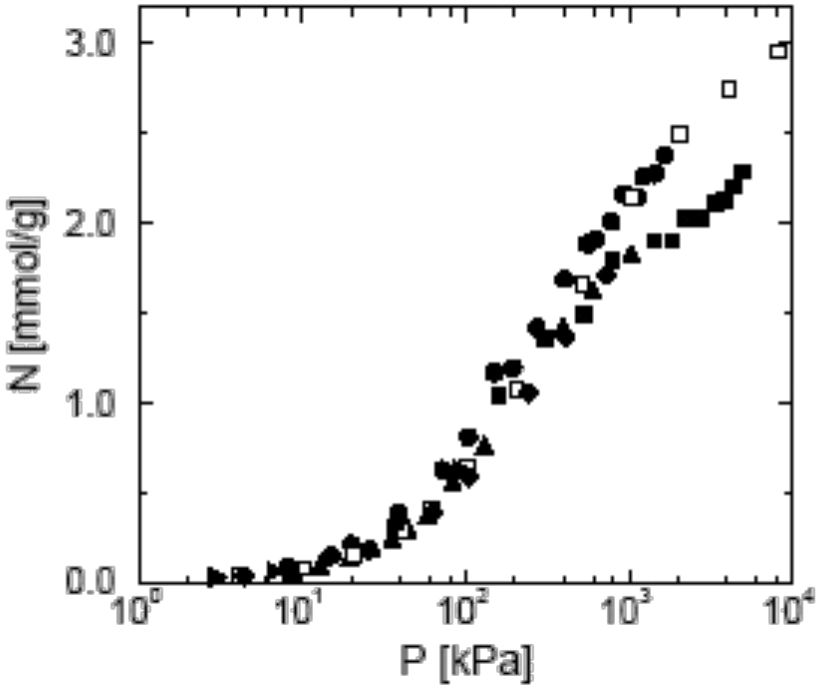
```
   SUBROUTINE mcexc                    attempt to exchange a particle
                                       with a reservoir
   if (ranf().lt.0.5) then             decide to remove or add a particle
     if (npart.eq.0) return            test whether there is a particle
     o=int(npart*ranf())+1             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
```

Application: equation of state of Lennard-Jones



Application: adsorption in zeolites





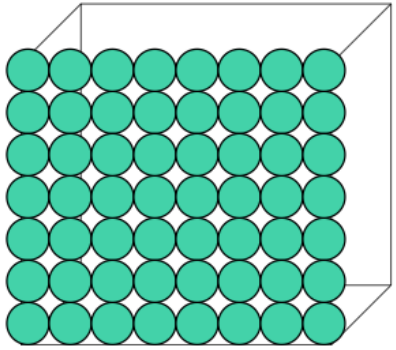
Summary

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

Practical Points

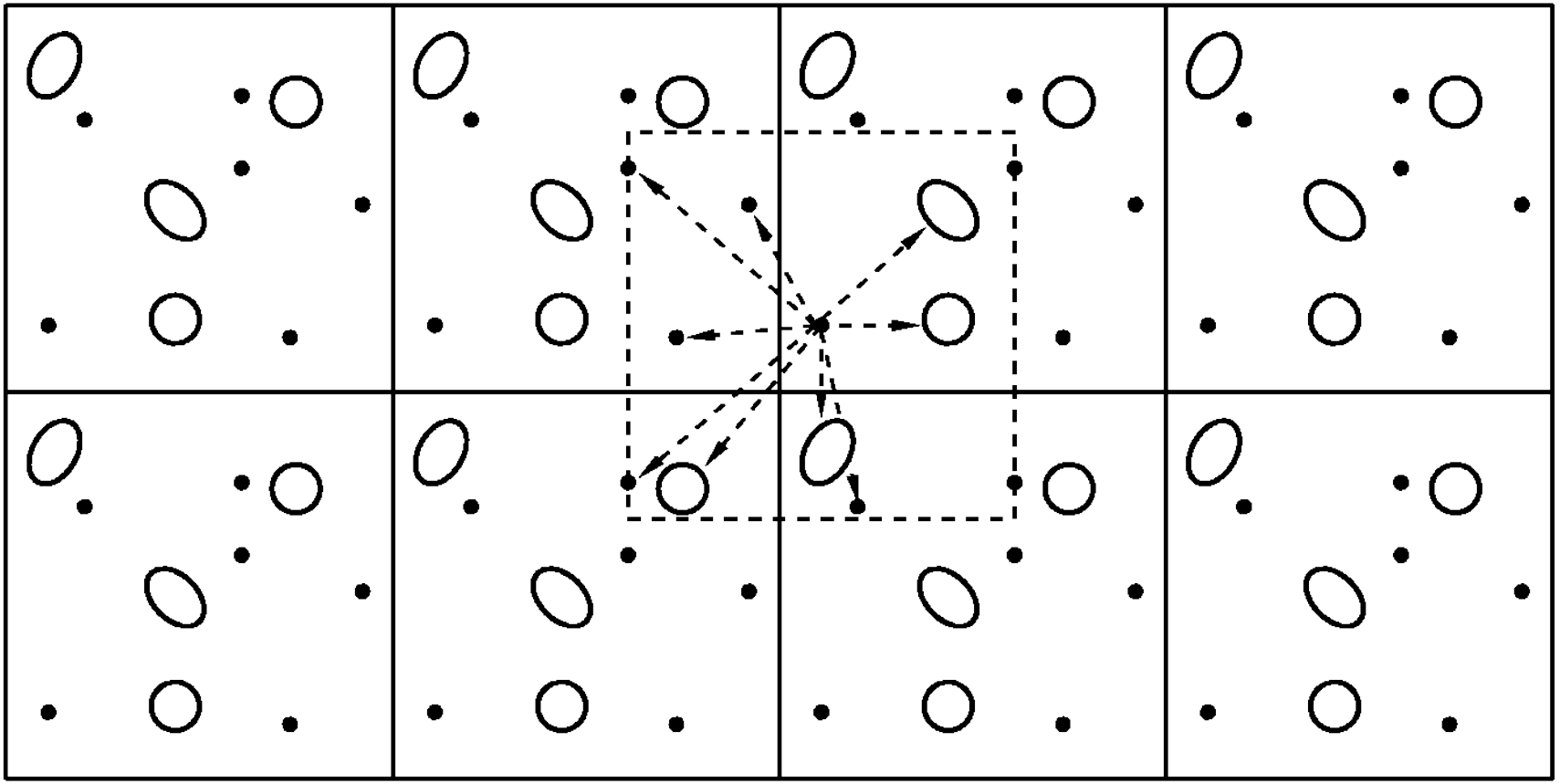
- Boundaries
- CPU saving methods
- Reduced units
- Long ranged forces

Boundary effects



- In small systems, boundary effects are always large.
- 1000 atoms in a simple cubic crystal – 488 boundary atoms.
- 1000000 atoms in a simple cubic crystal – still 6% boundary atoms.

Periodic boundary conditions



Algorithm 5 (Calculation of the energies)

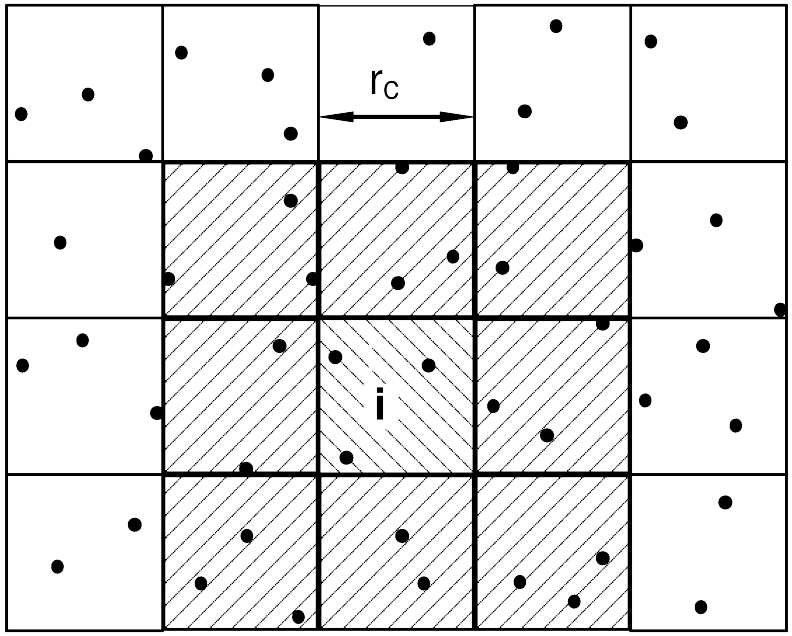
```
subroutine ener(x,en)                    determine the force
en=0                                     and energy
do i=1,npart
   f(i)=0                                set forces to zero
enddo
do i=1,npart-1
  do j=i+1,npart                         loop over all pairs
    xr=x(i)-x(j)
    xr=xr-box*nint(xr/box)               periodic boundary conditions
    r2=xr**2
    if (r2.lt.rc2) then                  test cutoff
      r2i=1/r2
      r6i=r2i**3
      ff=48*r2i*r6i*(r6i-0.5)            Lennard-Jones potential
      f(i)=f(i)+ff*xr                    update force
      f(j)=f(j)-ff*xr
      en=en+4*r6i*(r6i-1)-ecut           update energy
    endif
  enddo
enddo
return
end
```

Energy evaluation costs!

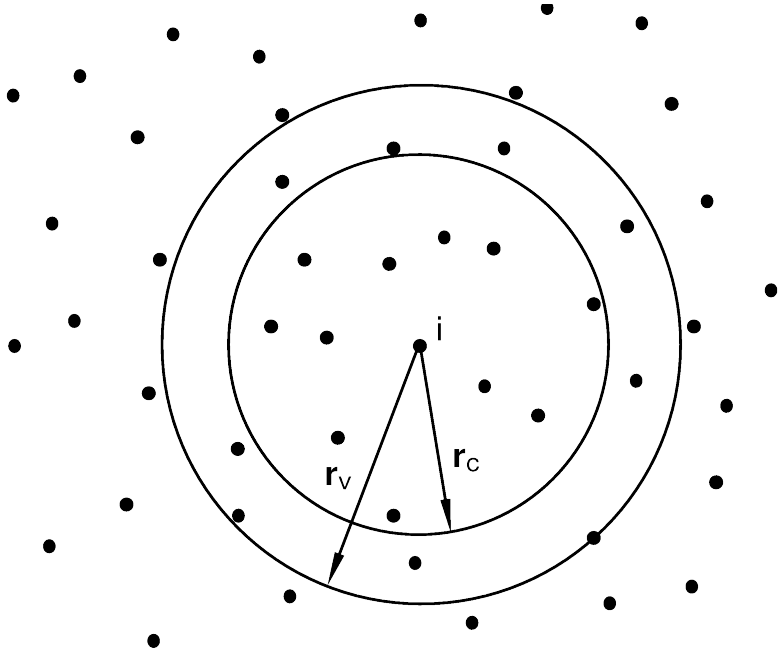
- The most time-consuming part of any simulation is the evaluation of all the interactions between the molecules.
- In general: $N(N-1)/2 = O(N^2)$
- But often, intermolecular forces have a short range:
- Therefore, we do not have to consider interactions with far- away atoms.

Saving CPU

- Cell list



Verlet List



Application: Lennard Jones potential

- The Lennard-Jones potential

$$u^{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

- The truncated Lennard-Jones potential

$$u(r) = \begin{cases} u^{LJ}(r) & r \le r_c \\ 0 & r > r_c \end{cases}$$

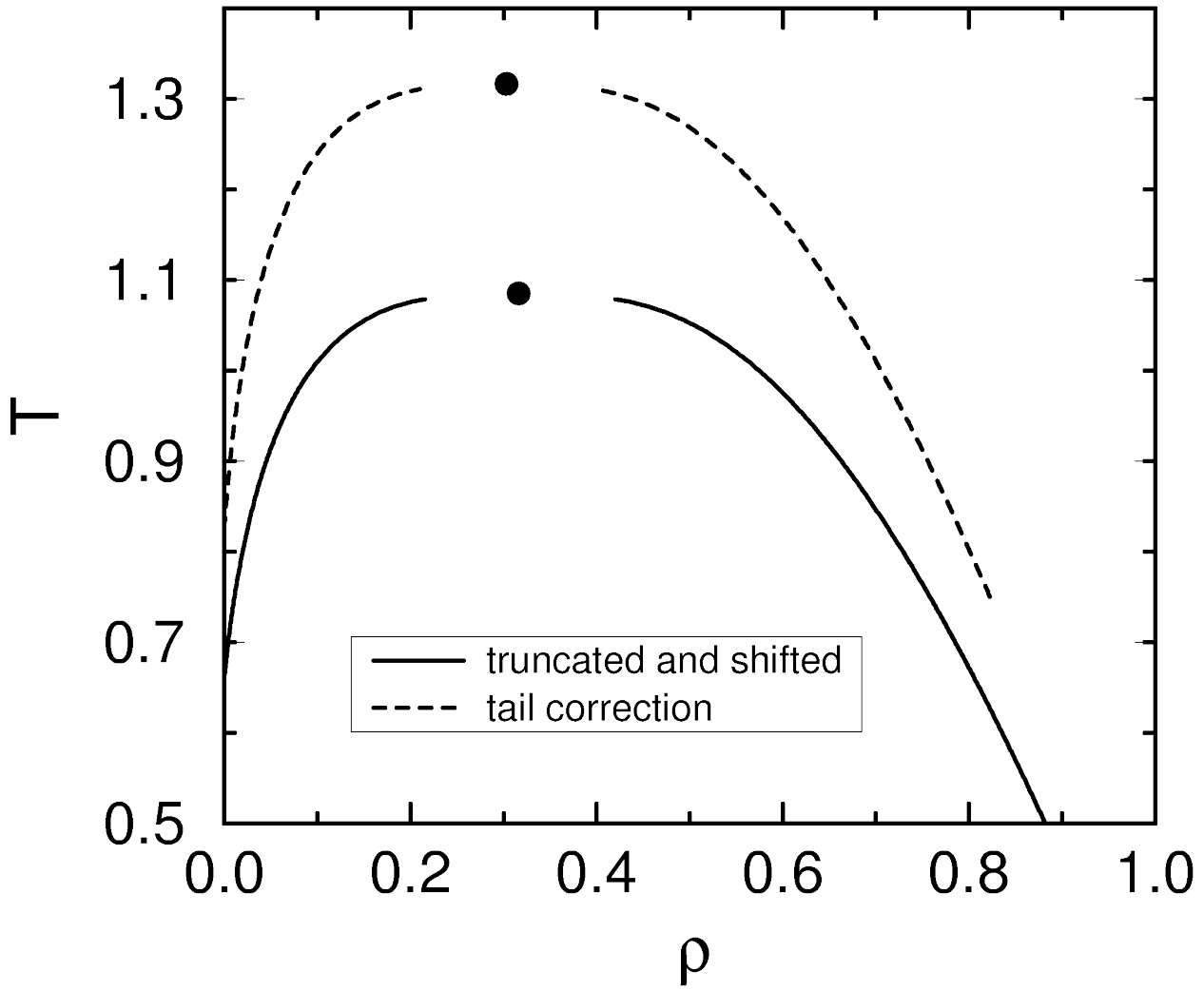
- The truncated and shifted Lennard-Jones potential

$$u(r) = \begin{cases} u^{LJ}(r) - u^{LJ}(r_c) & r \le r_c \\ 0 & r > r_c \end{cases}$$

Algorithm 5 (Calculation of the energies)

```
subroutine ener(x,en)                    determine the force
en=0                                     and energy
do i=1,npart
   f(i)=0                                set forces to zero
enddo
do i=1,npart-1
  do j=i+1,npart                         loop over all pairs
     xr=x(i)-x(j)
     xr=xr-box*nint(xr/box)              periodic boundary conditions
     r2=xr**2
     if (r2.lt.rc2) then                 test cutoff
        r2i=1/r2
        r6i=r2i**3
        ff=48*r2i*r6i*(r6i-0.5)          Lennard-Jones potential
        f(i)=f(i)+ff*xr                  update force
        f(j)=f(j)-ff*xr
        en=en+4*r6i*(r6i-1)-ecut         update energy
     endif
  enddo
enddo
return
end
```

Phase diagrams of Lennard Jones fluids



Long ranged interactions

- Long-ranged forces require special techniques.
  - Coulomb interaction (1/r in 3D)
  - Dipolar interaction ($1/r^3$ in 3D)

- ...and, in a different context:
  - Interactions through elastic stresses (1/r in 3D)
  - Hydrodynamic interactions (1/r in 3D)
  -

Reduced units

Example: Particles with mass **m** and pair potential:

$$v(r) = \epsilon f(r/\sigma)$$

Unit of length:	σ
Unit of energy:	ε
Unit of time:	$\sigma\sqrt{m/\epsilon}$

Beyond standard MC

- **Non Boltzmann Sampling – Lecture 2**
- **Parallel tempering**

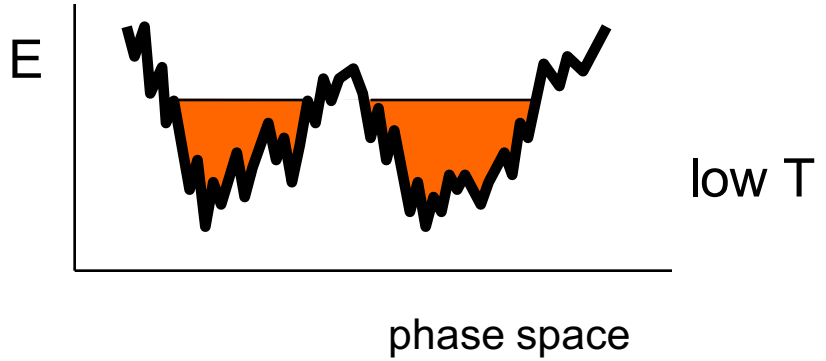
More to Come
Tomorrow
(Daan Frenkel)

Parallel tempering/Replica Exchange

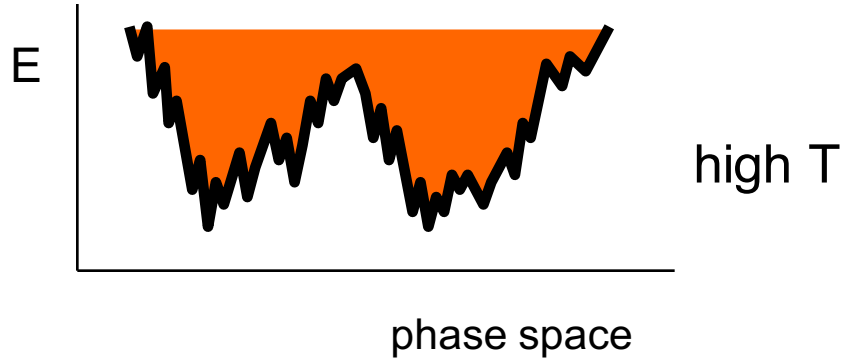
Ergodicity problems can occur, especially in glassy systems: biomolecules, molecular glasses, gels, etc.

The solution: go to high temperature

High barriers in energy landscape: difficult to sample



Barriers effectively low: easy to sample



Parallel tempering/Replica Exchange

Simulate two systems simultaneously

system 1
temperature T_1

system 2
temperature T_2

$$e^{-\beta_1 U_1(r^N)}$$

$$e^{-\beta_2 U_2(r^N)}$$

total Boltzmann weight:

$$e^{-\beta_1 U_1(r^N)} e^{-\beta_2 U_2(r^N)}$$

Swap move

- Allow two systems to swap

system 2
temperature T_1

system 1
temperature T_2

$$e^{-\beta_1 U_2(r^N)}$$

$$e^{-\beta_2 U_1(r^N)}$$

total Boltzmann weight:

$$e^{-\beta_1 U_2(r^N)} e^{-\beta_2 U_1(r^N)}$$

Acceptance rule

The ratio of the new Boltzmann factor over the old one is

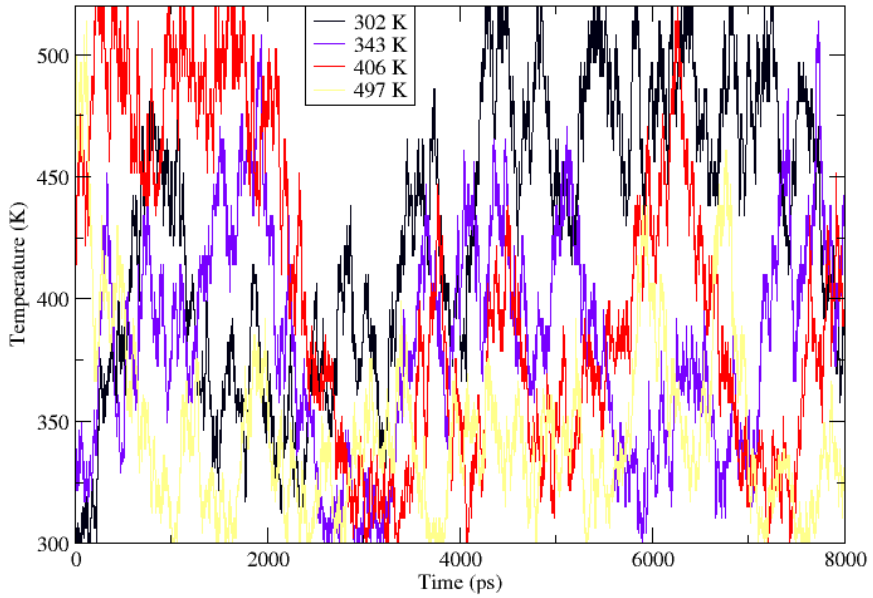
$$\frac{\mathcal{N}(n)}{\mathcal{N}(o)} = e^{(\beta_2-\beta_1)[U_2(r^N)-U_1(r^N)]}$$

The swap acceptance ratio is

$$\mathrm{acc}(1 \leftrightarrow 2) = \min\left(1, e^{(\beta_2-\beta_1)[U_2(r^N)-U_1(r^N)]}\right)$$

More replicas

Consider M replica's in the NVT ensemble at a different temperature.



A swap between two systems of different temperatures (T_i, T_j) is accepted if their potential energies are near.

other parameters can be used: Hamiltonian exchange

Questions

...

Lunch