Ensembles
Free Energies
Phase Transitions

Monte Carlo: Chapter 5
Molecular Dynamics: Chapter 6
Free Energies: Chapter 7

Classical and Statistical Thermodynamics

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

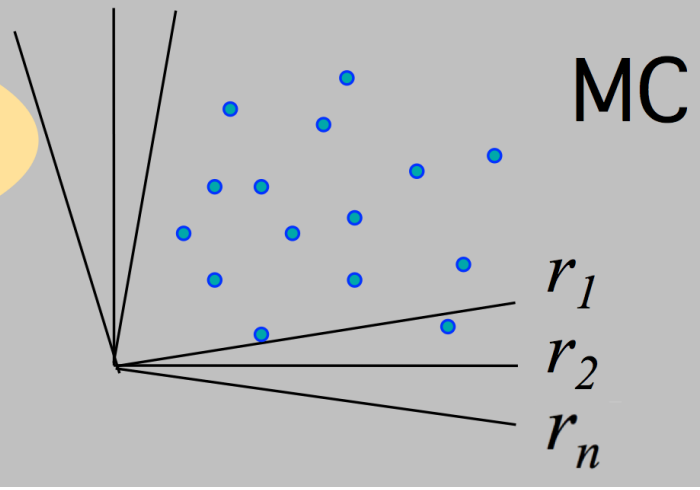
- Statistical Thermodynamics
  - The probability to find a particular configuration
  - Properties are expressed in term of averages
  - Free energies
- Thermodynamics: relation of the free energies to thermodynamic properties

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?

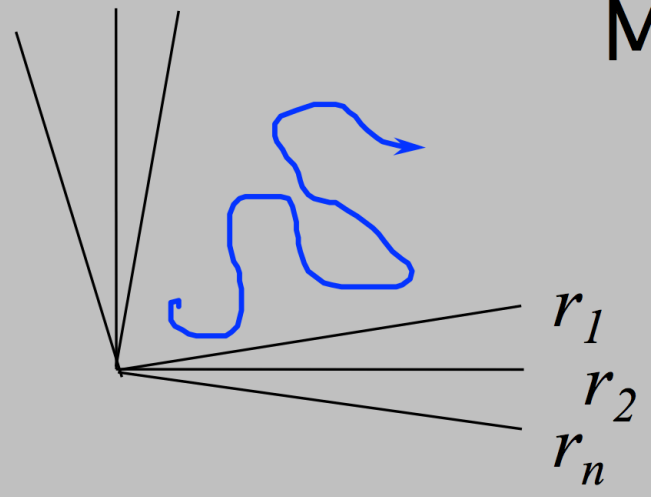


Molecular Dynamics

MD

- Theory:

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



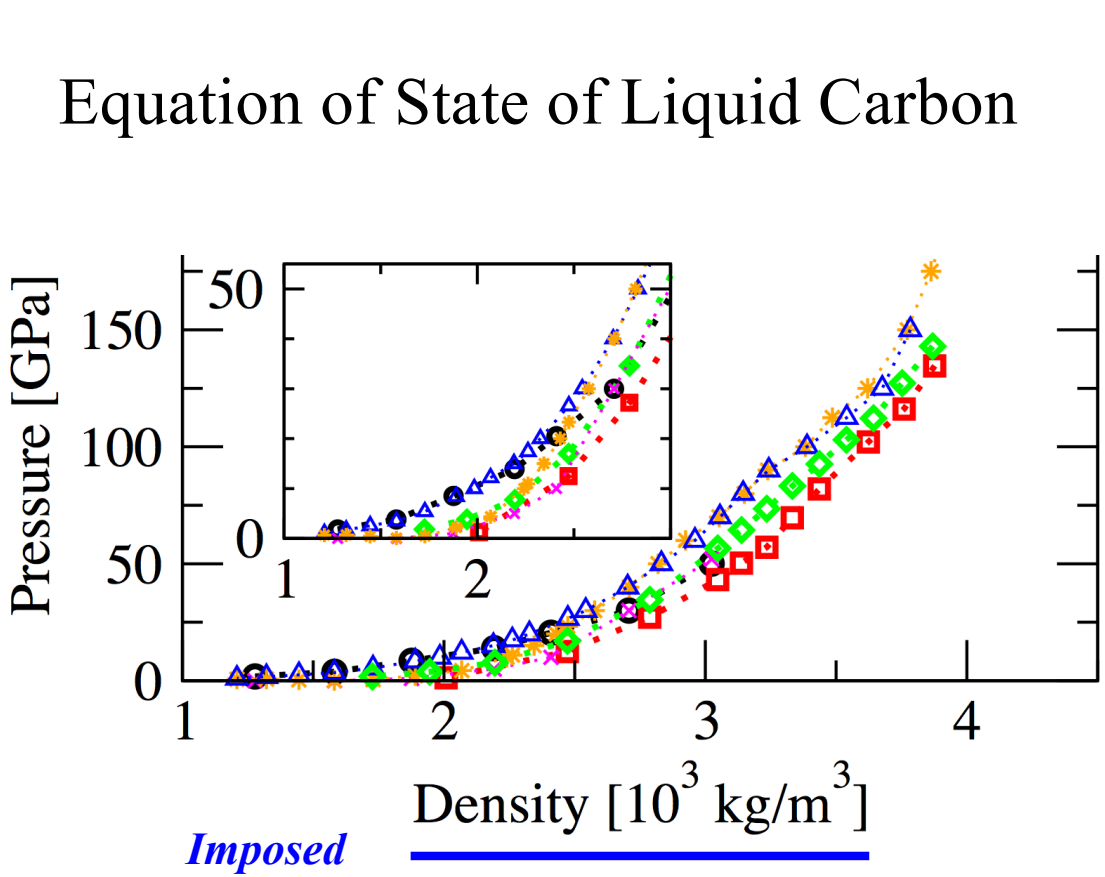
- Compute the forces on the particles
- Solve the equations of motion
- Sample after some timesteps

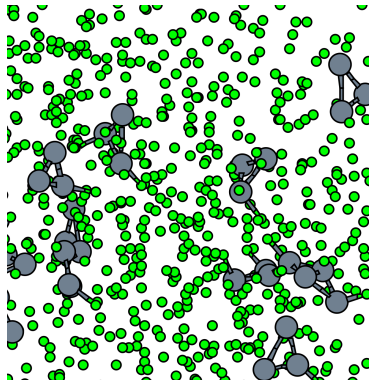
Different Ensembles

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
Pressure [GPa]
150
100
50
0
50
0
1
2
1
2
3
4
Density [10^3 kg/m^3]
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	α=6.74750993						
V_A	B_1^{sr}=27618.35706	β_1=6.34503890	B_2^{sr}=34.07142502	β_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}		$F_{ij,0}^{conj}$				$F_{ij,1}^{conj}$		
	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
A_{ij}	α_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}

τ_0=3.715735	ϵ_1=0.002827918	λ_1=1.338162	λ_2=2.260479	For ϵ_1, v_1, and v_2 see text.

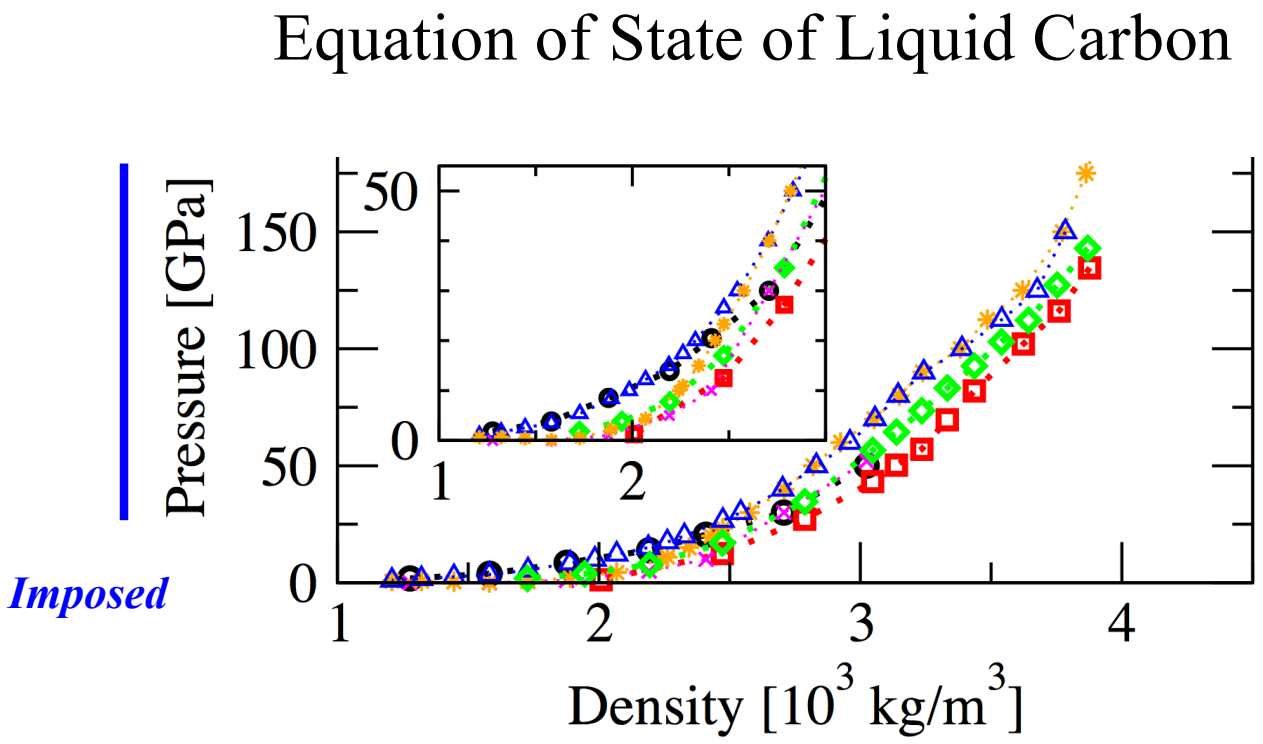
Middle-range potential V^{mr}

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

Impl

NPT

Liquids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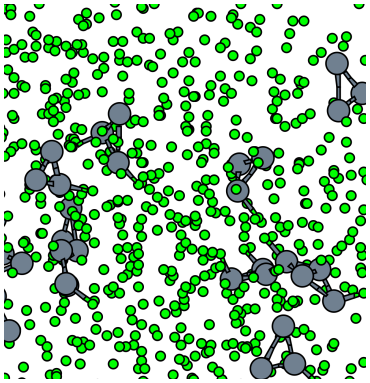
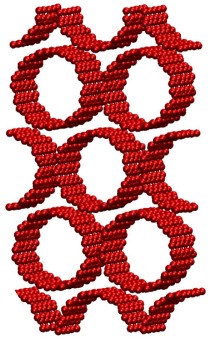
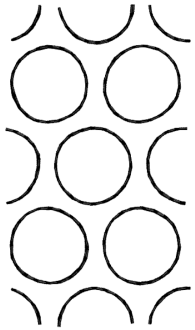


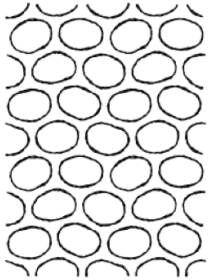
NPT

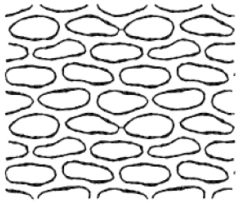
Non-Isotropic Systems
e.g. Solids

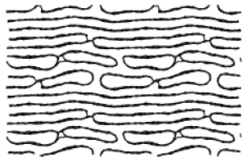
Structure and Transformation of
Carbon Nanotube Arrays

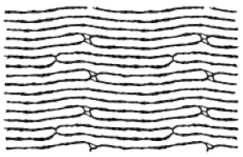


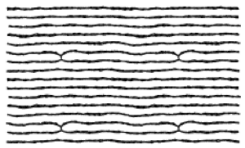








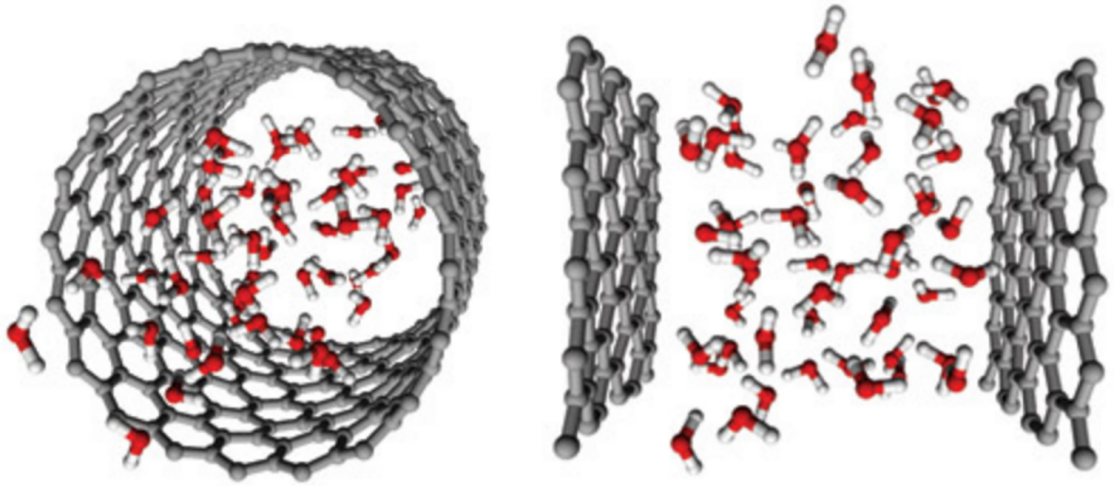




μVT

Adsorption

Adsorption in Carbon Nanostructues



Schwegler et al.

Statistical Thermodynamics

Partition function

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

Free energy

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

Ensemble average

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

Lecture 2

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:

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

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

Weighted Distribution

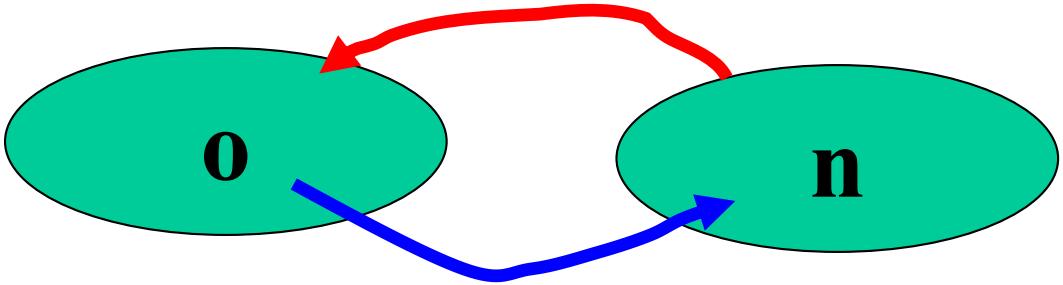
with

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

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

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

Monte Carlo: Detailed balance



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

NVT-ensemble

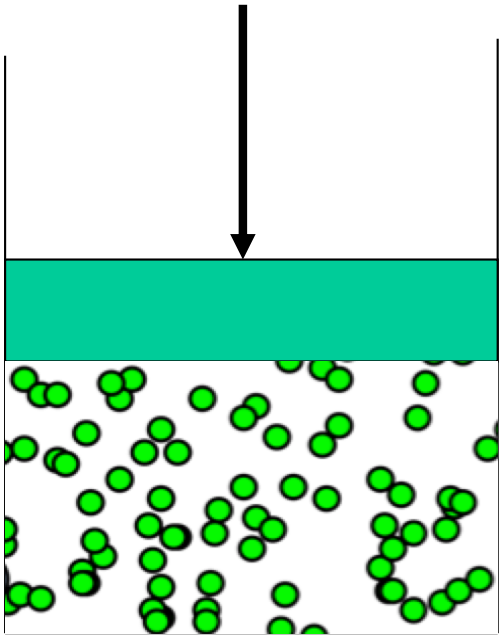
$$N(n) \propto \exp\left[-\beta U(n)\right]$$

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

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

Realize by, for example, Metropolis algorithm

NPT ensemble



We control the

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

Intermezzo

Scaled coordinates

Partition function

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

Scaled coordinates

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

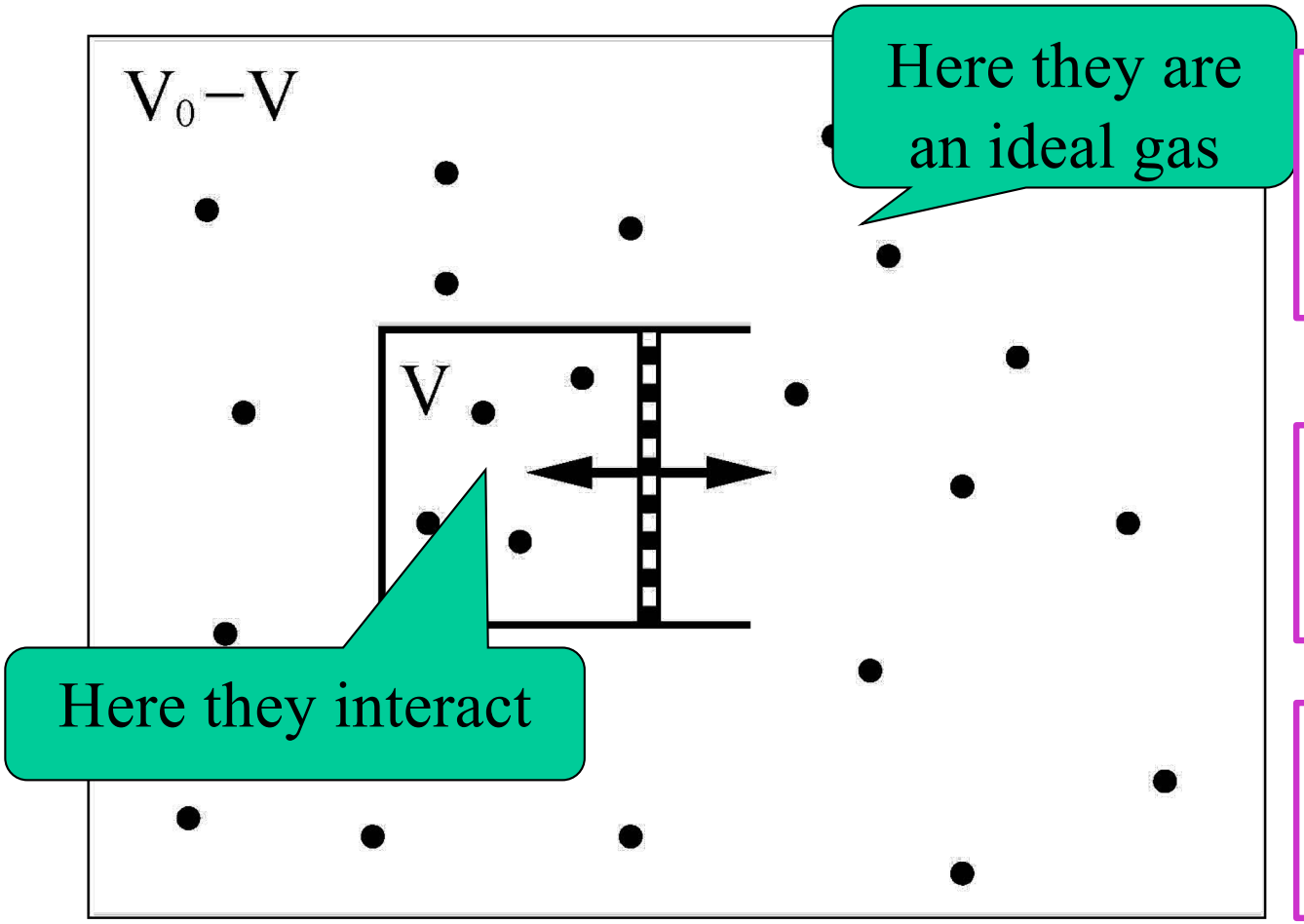
This gives for the partition function

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

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

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

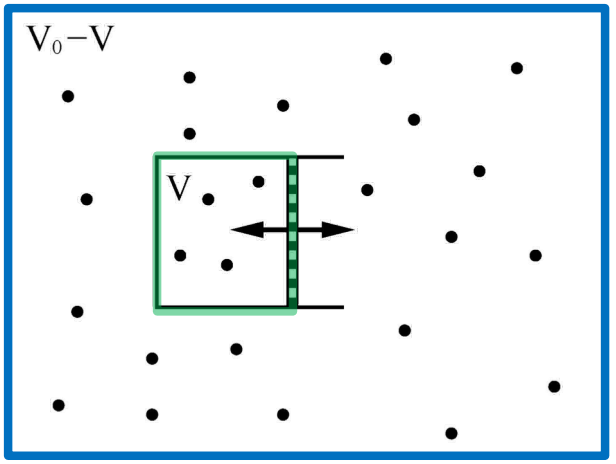
V_0 is fixed

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:

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

NPT Ensemble

Partition function:

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

Probability to find a particular configuration:

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

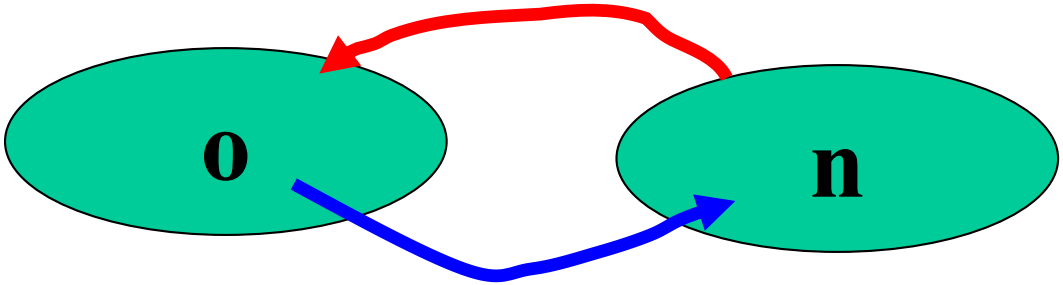
Sample a particular c

- change of volum
- change of reduced

Acceptance rules ??

Detailed balance

Detailed balance



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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

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

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

NPT-ensemble

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

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

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

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

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

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:

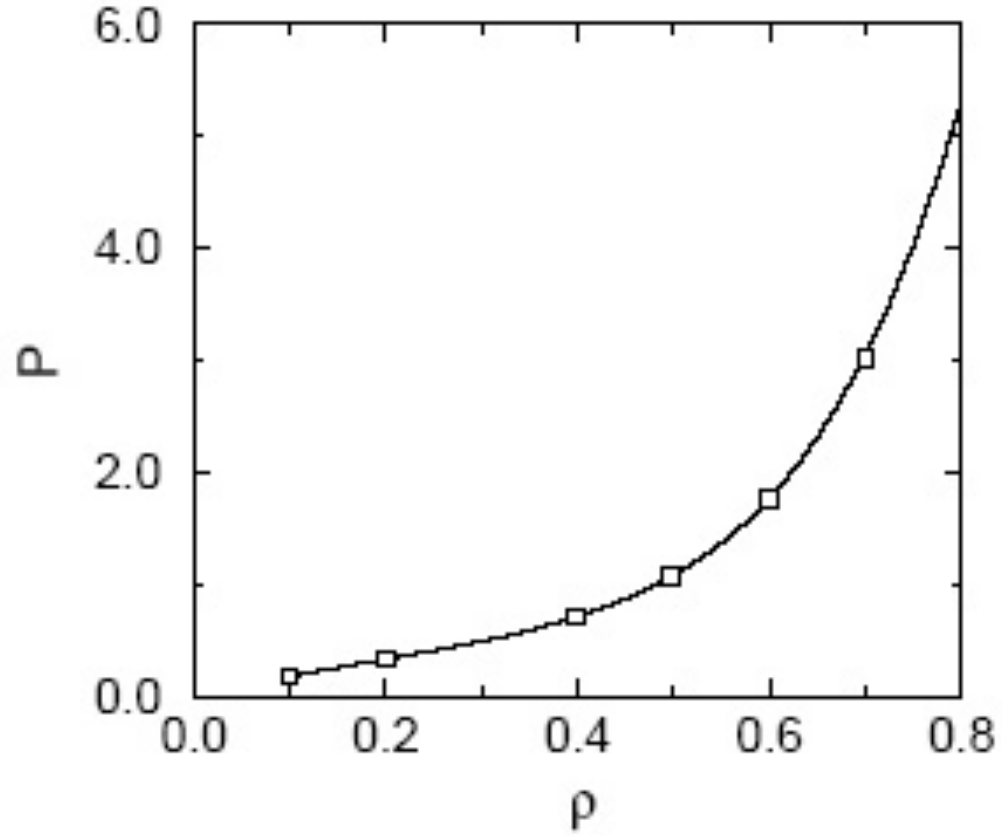
1. *Subroutine* `ener` *calculates the energy of a particle at the given position.*
2. *Note that, if a configuration is rejected, the old configuration is retained.*
3. *The* `ranf()` *is a random number uniform in* [0, 1].

Algorithm 11 (Attempt to Change the Volume)

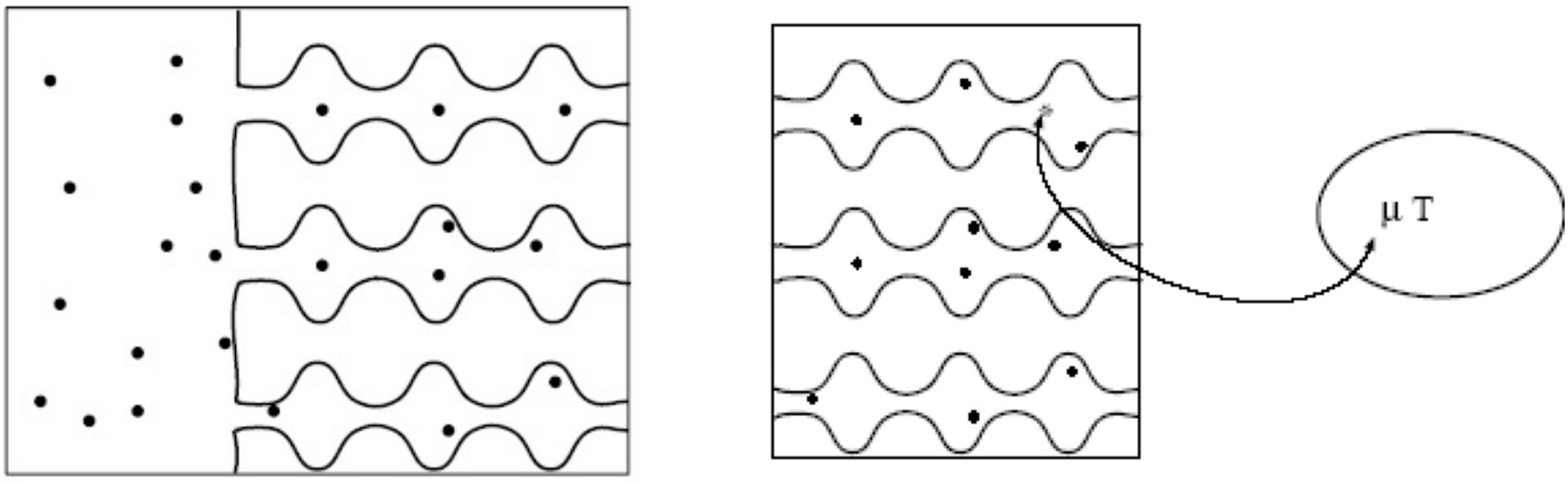
```
SUBROUTINE mcvol                                  attempts to change
                                                  the volume
call toterg(box,eno)                              total energy old conf.
vo=box**3                                         determine old volume
lnvn=log(vo)+(ranf()-0.5)*vmax                    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

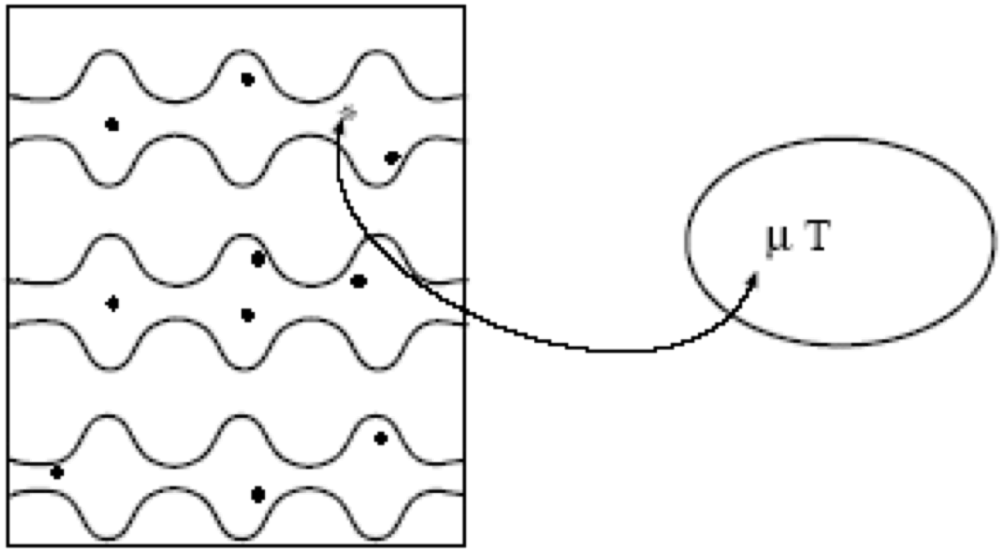


Grand-canonical ensemble



What are the equilibrium conditions?

Grand-canonical ensemble

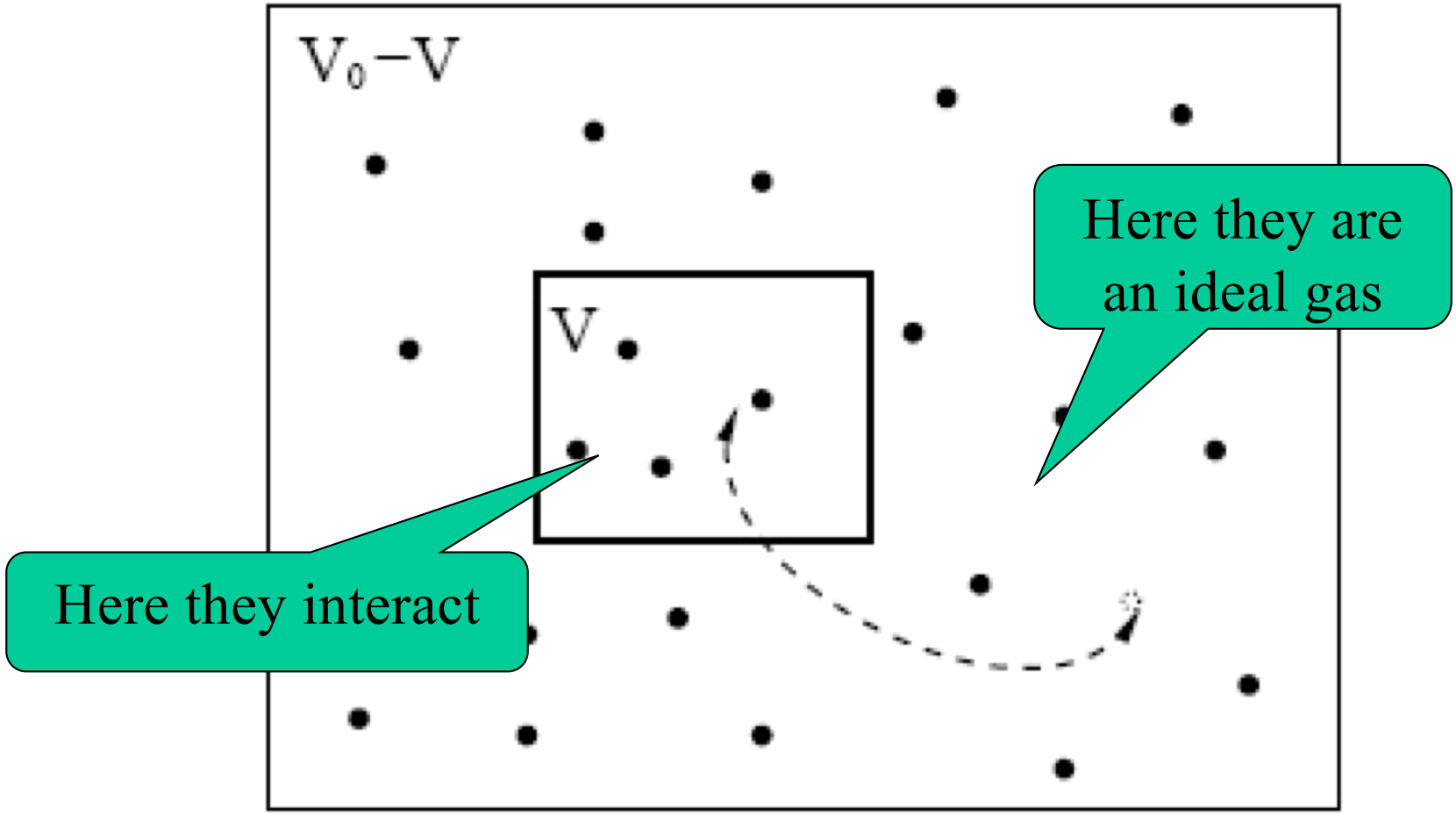


We impose:

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

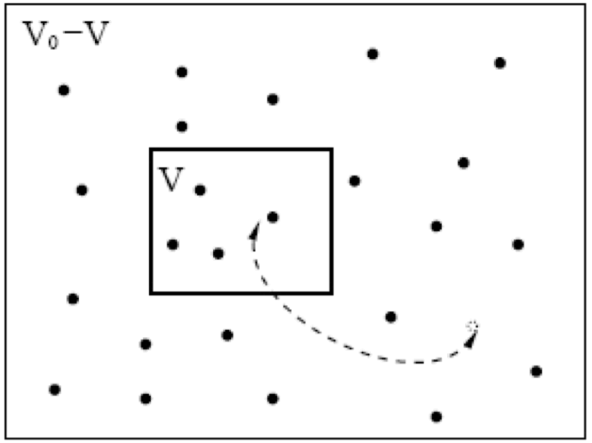
- But **NOT** pressure

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:

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

Probability to find a particular configuration:

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

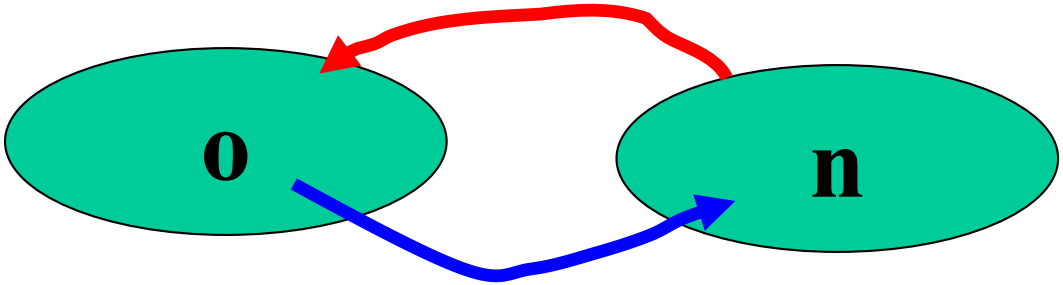
Sample a particular c

- Change of the nu
- Change of reduce

Acceptance rules ??

Detailed balance

Detailed balance



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

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

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

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

μVT-ensemble

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

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

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

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

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

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
```

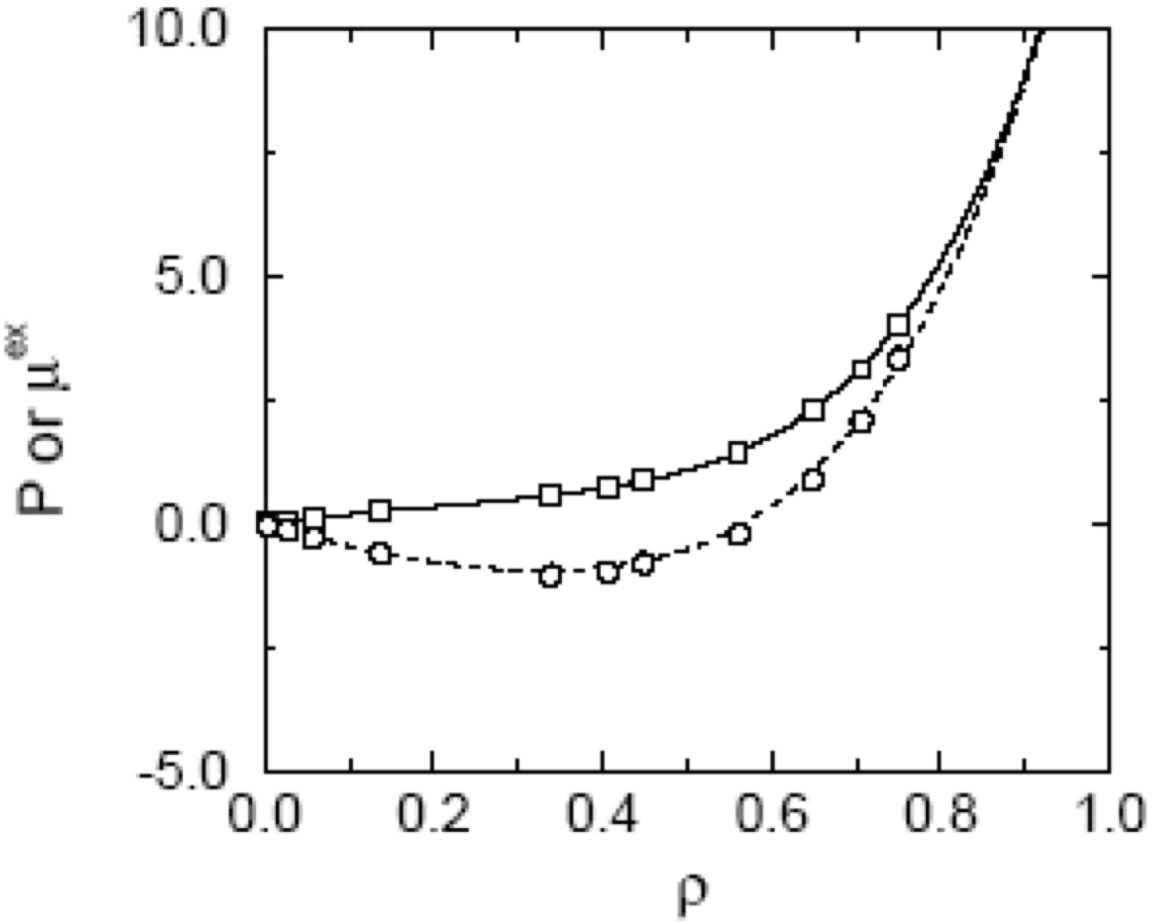
Comments to this algorithm:

1. *This algorithm ensures that, after each MC step, detailed balance is obeyed. Per cycle we perform on average* `npav` *attempts*[b] *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



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	$\beta\Omega=-\ln Q(\mu,V,T)=-\beta PV$

with Monte Carlo

Molecular Dynamics Ensembles

NVT
Constant Temperature

Velocity scaling
Andersen Thermostat
Hamiltonian & Lagrangian Appendix A
Nose-Hoover thermostat

Constant Temperature
Naïve approach

Velocity scaling

$$\frac{3}{2}k_B T = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}mv_i^2$$

$$v_i \rightarrow v_i\sqrt{\frac{T_{\text{req}}}{\text{T}}}$$

Do we sample the canonical ensemble?

Partition function

$$Q_{NVT} = \frac{1}{h^{3N} N!} \int \mathrm{d}\mathrm{p}^N \exp\left[-\beta \sum p_i^2 / 2m\right] \int \mathrm{d}\mathrm{r}^N \exp\left[-\beta U\left(\mathrm{r}^N\right)\right]$$

Maxwell-Boltzmann velocity distribution

$$P(p) = \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left[-\beta p^2 / 2m\right]$$

$$\left\langle p^2 \right\rangle = \int \mathrm{d}\mathrm{p} P(p)\, p^2$$

$$= \left(\frac{\beta}{2\pi m}\right)^{3/2} \int \mathrm{d}p 4\pi p^4 \exp\left[-\beta p^2 / 2m\right]$$

$$= \frac{3m}{\beta}$$

$$P(p)=\left(\frac{\beta}{2\pi m}\right)^{3/2}\exp\left[-\beta p^2/2m\right]$$

$$\left\langle p^2\right\rangle=\int \mathrm{d}pP(p)\,p^2=\left(\frac{\beta}{2\pi m}\right)^{3/2}\int \mathrm{d}p 4\pi p^4\exp\left[-\beta p^2/2m\right]\quad=\frac{3m}{\beta}$$

$$\left\langle p^4\right\rangle=\int \mathrm{d}pP(p)\,p^4=15\left(\frac{m}{\beta}\right)^2$$

Fluctuations in the kinetic energy or particle

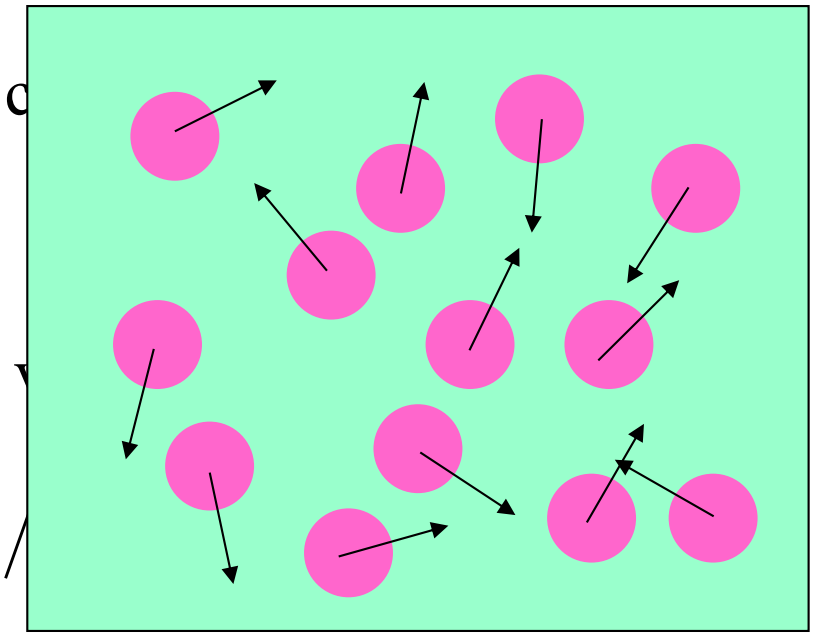
$$\frac{\sigma^2_{p^2}}{\left\langle p^2\right\rangle^2}=\frac{\left\langle p^4\right\rangle-\left\langle p^2\right\rangle^2}{\left\langle p^2\right\rangle^2}\quad=\frac{15\left(m/\beta\right)^2-\left(3m/\beta\right)^2}{\left(3m/\beta\right)^2}=\frac{2}{3}$$

Fluctuations in the temperature

$$\frac{\sigma^2_{k_BT}}{\left\langle k_BT\right\rangle^2}=\frac{\left\langle \left(k_BT\right)^2\right\rangle-\left\langle k_BT\right\rangle^2}{\left\langle k_BT\right\rangle^2}\quad=\frac{2}{3N}$$

Andersen thermostat

Every particle has a fixed probability to c
with the Andersen demon



After collision the particle is give a new v

$$P(v) = \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left[-\beta m v^2 /\right.$$

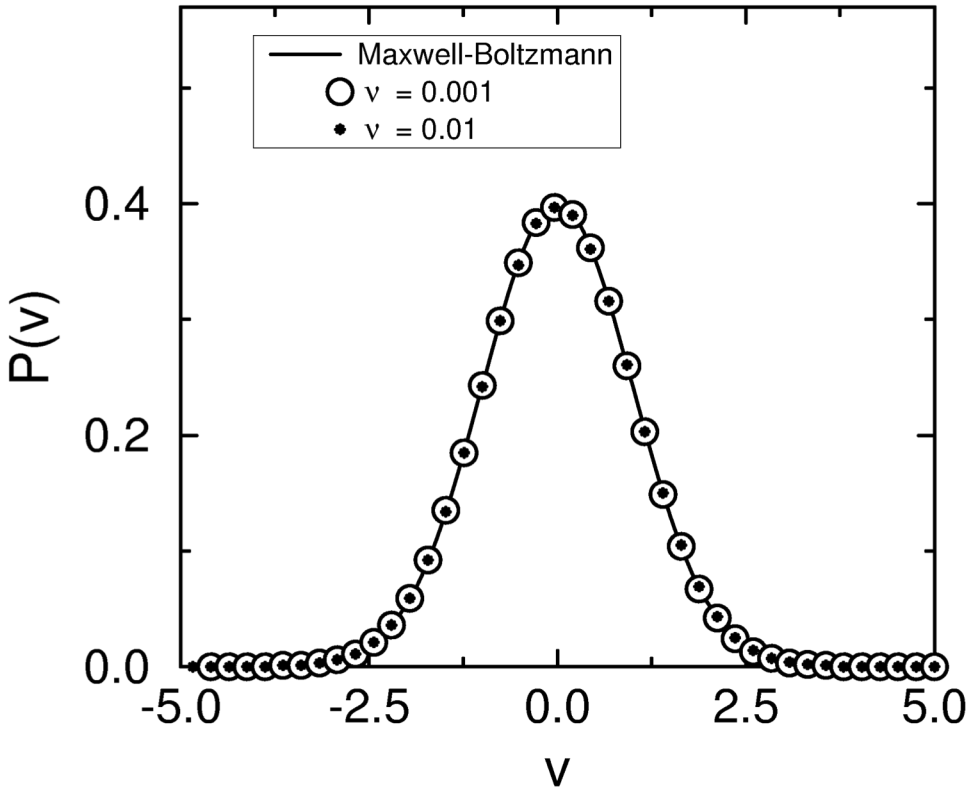
The probabilities to collide are uncorrelated (Poisson distribution)

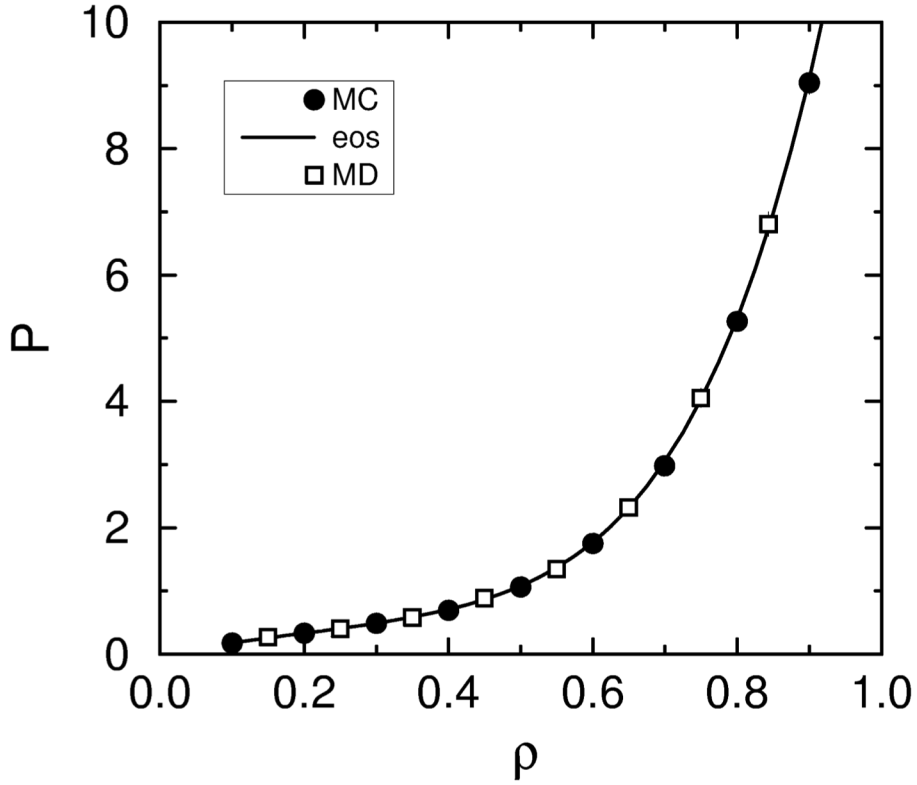
Distribution of time-intervals between collisions:

$$P(t;\nu) = \nu \exp\left[-\nu t\right]$$

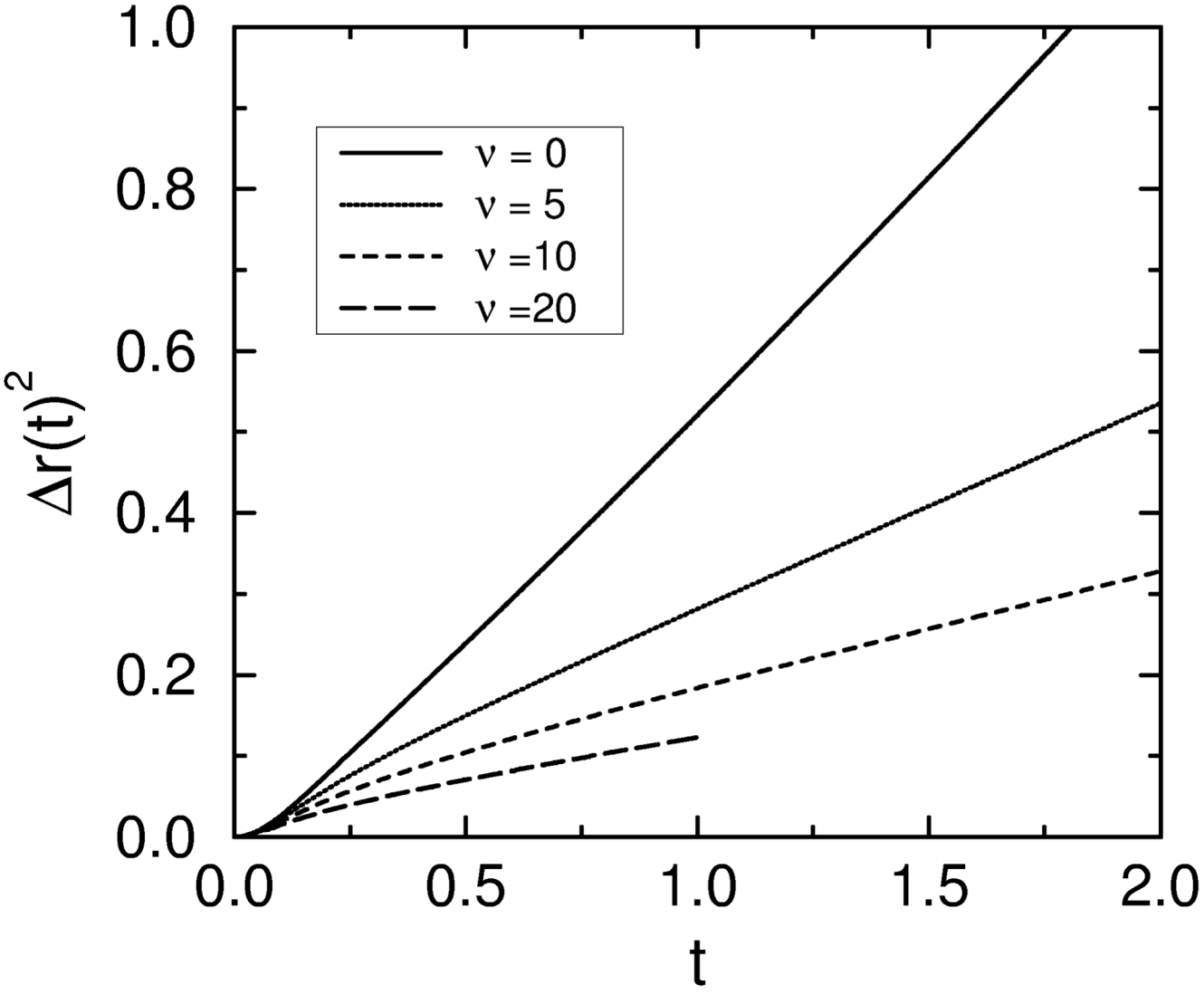
ν : collision frequency

Andersen thermostat: static properties





Andersen thermostat: dynamic properties



Equations of Motion
Hamiltonian and Lagrangian

Cartesian coordinates $\left(x,\dot{x}\right)$ (Newton) $\rightarrow$
Generalized coordinates $\left(q,\dot{q}\right)$

Lagrangian $L\left(q,\dot{q}\right)=U_k\left(\dot{q}\right)-U_p\left(q\right)$

$$\frac{d}{dt}\frac{\partial L\left(q,\dot{q}\right)}{\partial \dot{q}}=\frac{\partial L\left(q,\dot{q}\right)}{\partial q}$$

Lagrangian equations of motion

Conjugate momentum

$$p_q=\frac{\partial L\left(q,\dot{q}\right)}{\partial \dot{q}} \qquad \dot{p}_q=\frac{\partial L\left(q,\dot{q}\right)}{\partial q}$$

Newton?

$$L\left(q,\dot{q}\right)=U_k\left(\dot{q}\right)-U_p\left(q\right) \qquad \frac{d}{dt}\frac{\partial L\left(q,\dot{q}\right)}{\partial \dot{q}}=\frac{\partial L\left(q,\dot{q}\right)}{\partial q}$$

Valid in any coordinate system: Cartesian

$$L\left(x,\dot{x}\right)=\frac{1}{2}m\dot{x}^2-U_p\left(x\right)$$

Conjugate momentum

$$p_x=\frac{\partial L\left(x,\dot{x}\right)}{\partial \dot{x}}=m\dot{x}$$

$$\dot{p}_x=\frac{\partial L\left(x,\dot{x}\right)}{\partial x}=-\frac{\partial U_p\left(x\right)}{\partial x}=F$$

Lagrangian dynamics

We have:

2^{nd} order differential equation

$$\left(q,\dot{q}\right)\rightarrow\ddot{q}=\cdots$$

Two 1^{st} order diff

With these variables we can do statistical thermodynamics

Change dependence:

$$\left(q,\dot{q}\right)\rightarrow\left(q,p\right)$$

$$\left(q,\dot{q}\right)\rightarrow\left(q,p\right) \qquad p=\frac{\partial L\left(q,\dot{q}\right)}{\partial\dot{q}} \qquad \dot{p}=\frac{\partial L\left(q,\dot{q}\right)}{\partial q}$$

$$H\left(q,p\right)=\dot{q}p-L\left(q,\dot{q}\right) \qquad \text{Hamiltonian}$$

$$\mathrm{dH}\left(q,p\right)=\mathrm{d}\left(\dot{q}p\right)-\mathrm{dL}\left(q,\dot{q}\right)$$

$$=\dot{q}\mathrm{d}\left(p\right)+p\mathrm{d}\left(\dot{q}\right)-\left[\frac{\partial L\left(q,\dot{q}\right)}{\partial q}\mathrm{d}q+\frac{\partial L\left(q,\dot{q}\right)}{\partial\dot{q}}\mathrm{d}\dot{q}\right]$$

$$=-\dot{p}\mathrm{d}q+\dot{q}\mathrm{d}\left(p\right)$$

$$\mathrm{dH}\left(q,p\right)=\left(\frac{\partial H}{\partial q}\right)\mathrm{d}q+\left(\frac{\partial H}{\partial p}\right)\mathrm{d}p$$

$$\begin{cases}\dot{q}=\dfrac{\partial H}{\partial p}\\[2ex]\dot{p}=-\dfrac{\partial H}{\partial q}\end{cases}$$

Hamilton's equations of motion

Nosé thermostat

Lagrangian

$$L_{\text{Nose}} = \sum_{i=1}^{N} \frac{1}{2} m s^2 \dot{r}_i^2 - U\left(r^N\right) + \frac{1}{2} Q \dot{s}^2 - \frac{g}{\beta} \ln s$$

Extended system 3N+1 variables

Conjugate momentum

$$p_i = \frac{\partial L}{\partial \dot{r}_i} = m s^2 \dot{r}_i \qquad p_s = \frac{\partial L}{\partial \dot{s}} = Q \dot{s}$$

Associated mass

Hamiltonian

$$H_{\text{Nose}} = \sum_{i=1}^{N} \dot{r}_i p_i + \dot{s} p_s - L$$

$$H_{\text{Nose}} = \sum_{i=1}^{N} \frac{p_i^2}{2 m s^2} + \frac{p_s}{2Q} + U\left(r^N\right) + \frac{g}{\beta} \ln s$$

$$p' = p/s$$

$$= H\left(p', r\right) + \frac{p_s}{2Q} + \frac{g}{\beta} \ln s$$

$$\delta\left(h(s)\right)=\frac{\delta\left(s-s_0\right)}{h'(s)}$$

H

Recall $\delta\left(H\left(p',r\right)+\frac{p_s^2}{2Q}+\frac{g}{\beta}\ln s-E\right)$

Q_{No} $\left(H\left(p',r\right)+\frac{p_s^2}{2Q}+\frac{g}{\beta}\ln s-E\right)$

MD $Q_{NVE}=\frac{1}{N!}\int \mathrm{d}p^N\int \mathrm{d}r^N\,\delta\left(E-H\left(r^N,p^N\right)\right)$

$h(s)=H\left(p',r\right)+\frac{p_s^2}{2Q}+\frac{g}{\beta}\ln s-E$

MC $Q_{NVT}=\frac{1}{N!}\int \mathrm{d}p^N\int \mathrm{d}r^N\exp\left[-\beta H\left(r^N,p^N\right)\right]$

$=\frac{h'(s)}{N!}\int \mathrm{d}\frac{g}{\beta}\int \mathrm{d}p'^N\int_0^\infty \mathrm{d}s\,s^{3N+1}\exp\left\{\frac{\beta}{g}\left[E-H\left(p',r\right)-\frac{p_s^2}{2Q}\right]\right\}\delta\left(s-e^{\frac{\beta}{g}\left[E-H\left(p',r\right)-\frac{p2_s}{2Q}\right]}\right)$

Gaussian integral

$=\frac{1}{N!}\int \mathrm{d}p\frac{\beta_s}{g}\int \mathrm{d}p'^N\int \mathrm{d}r^N\frac{\beta}{g}e^{\frac{\beta}{g}\left[E-H\left(p',r\right)-\frac{p_s^2}{2Q}\right](3N+1)}\left(e^{\frac{\beta}{g}\left[E-H\left(p',r\right)-\frac{p2_s}{2Q}\right]}\right)^{3N+1}$

$=\frac{C}{N!}\int \mathrm{d}p'^N\int \mathrm{d}r^N e^{-\frac{\beta(3N+1)}{g}H\left(p',r\right)}$ $\qquad g=3N+1$

$=\frac{C}{N!}\int \mathrm{d}p'^N\int \mathrm{d}r^N e^{-\beta H\left(p',r\right)}$

Equations of Motion

Lagrangian

$$L_{\text{Nose}} = \sum_{i=1}^{N} \frac{1}{2} m s^2 \dot{r}_i^2 - U\left(r^N\right) - \frac{1}{2} Q \dot{s}^2 - \frac{g}{\beta} \ln s$$

Hamiltonian

$$H_{\text{Nose}} = \sum_{i=1}^{N} \frac{p_i^2}{2ms^2} + \frac{p_s^2}{2Q} + U\left(r^N\right) + \frac{g}{\beta} \ln s$$

Conjugate momenta

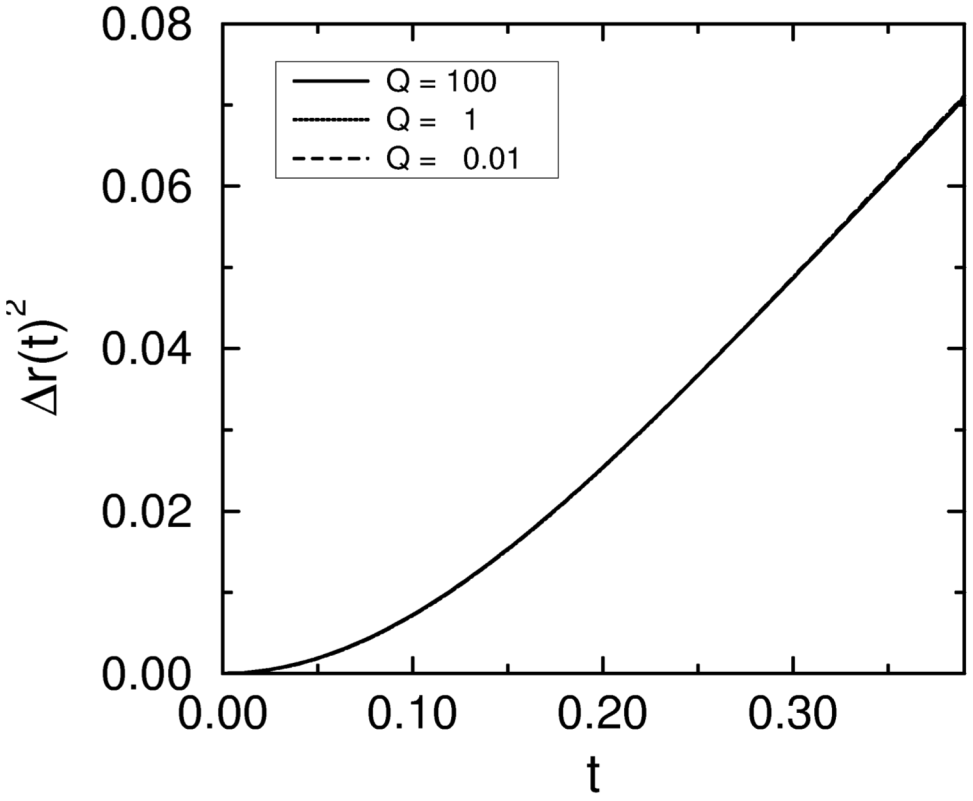
$$p_i = \frac{\partial L}{\partial \dot{r}_i} = m s^2 \dot{r}_i \qquad p_s = \frac{\partial L}{\partial \dot{s}} = Q \dot{s}$$

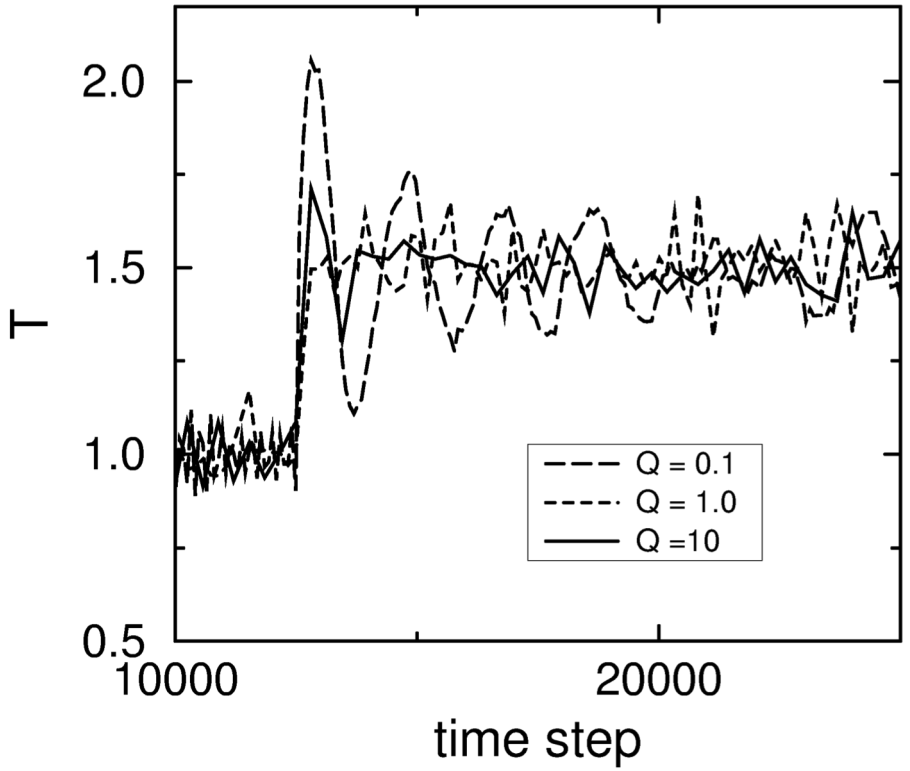
Equations of motion:

$$\frac{\mathrm{d}r_i}{\mathrm{d}t} = \frac{\partial H_{\text{Nose}}}{\partial p_i} = \frac{p_i}{ms^2} \qquad \frac{\mathrm{d}p_i}{\mathrm{d}t} = -\frac{\partial H_{\text{Nose}}}{\partial r_i} = -\frac{\partial U\left(r^N\right)}{\partial r_i}$$

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{\partial H_{\text{Nose}}}{\partial p_s} = \frac{p_s}{Q} \qquad \frac{\mathrm{d}p_s}{\mathrm{d}t} = -\frac{\partial H_{\text{Nose}}}{\partial s} = \frac{1}{s}\left(\sum \frac{p_i^2}{ms^2} - \frac{g}{\beta}\right)$$

Nosé - Hoover


0.08
0.06
0.04
0.02
0.00
0.00
0.10
0.20
0.30
t
$\Delta r(t)^2$
Q = 100
Q = 1
Q = 0.01


2.0
1.5
1.0
0.5
10000
20000
time step
T
Q = 0.1
Q = 1.0
Q =10