

# Computer simulation of molecular systems

**FEEG6016**

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# Computer simulation of molecular systems

- Statistical mechanics
  - Monte Carlo simulations
  - Molecular dynamics
  - Simple interaction potentials
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- Allen and Tildesley “Computer Simulation of Liquids”  
Oxford, 1989
  - Frenkel and Smit “Understanding Molecular  
Simulation”, Academic Press, 1996

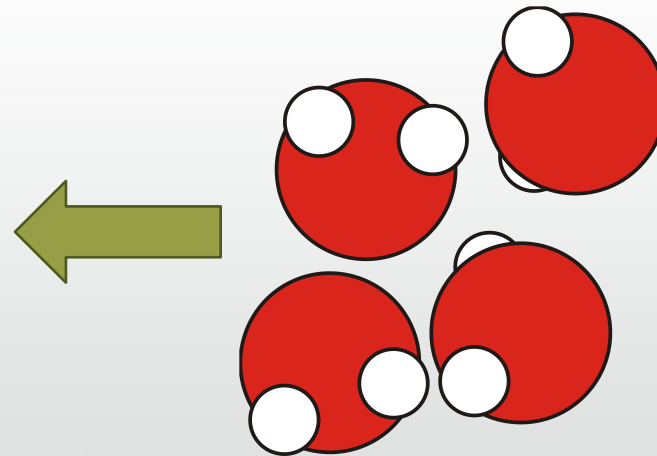
# Macroscopic vs. microscopic

- A system is characterised by a few macroscopic variables (temperature, pressure, density).
- A system is characterised by many microscopic variables (positions and velocities of  $10^{23}$  atoms).

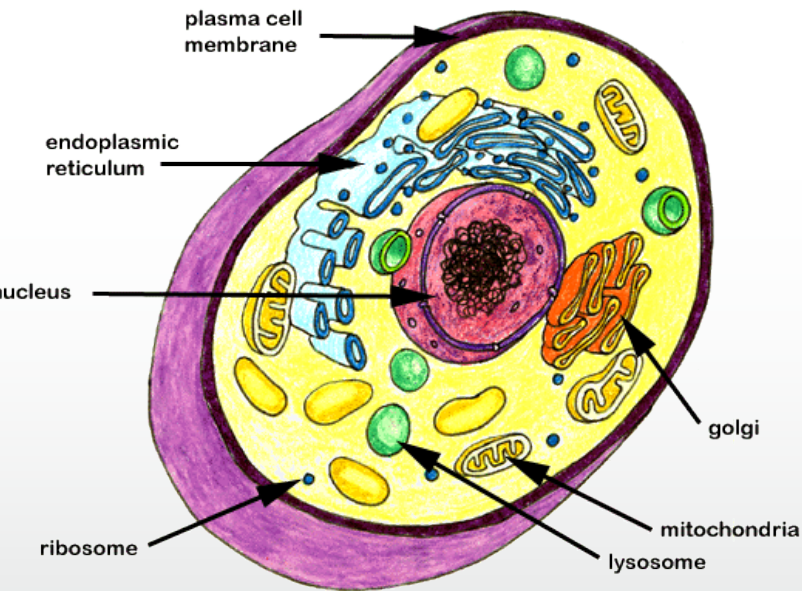
This is what we simulate...



While this is what we  
want to calculate

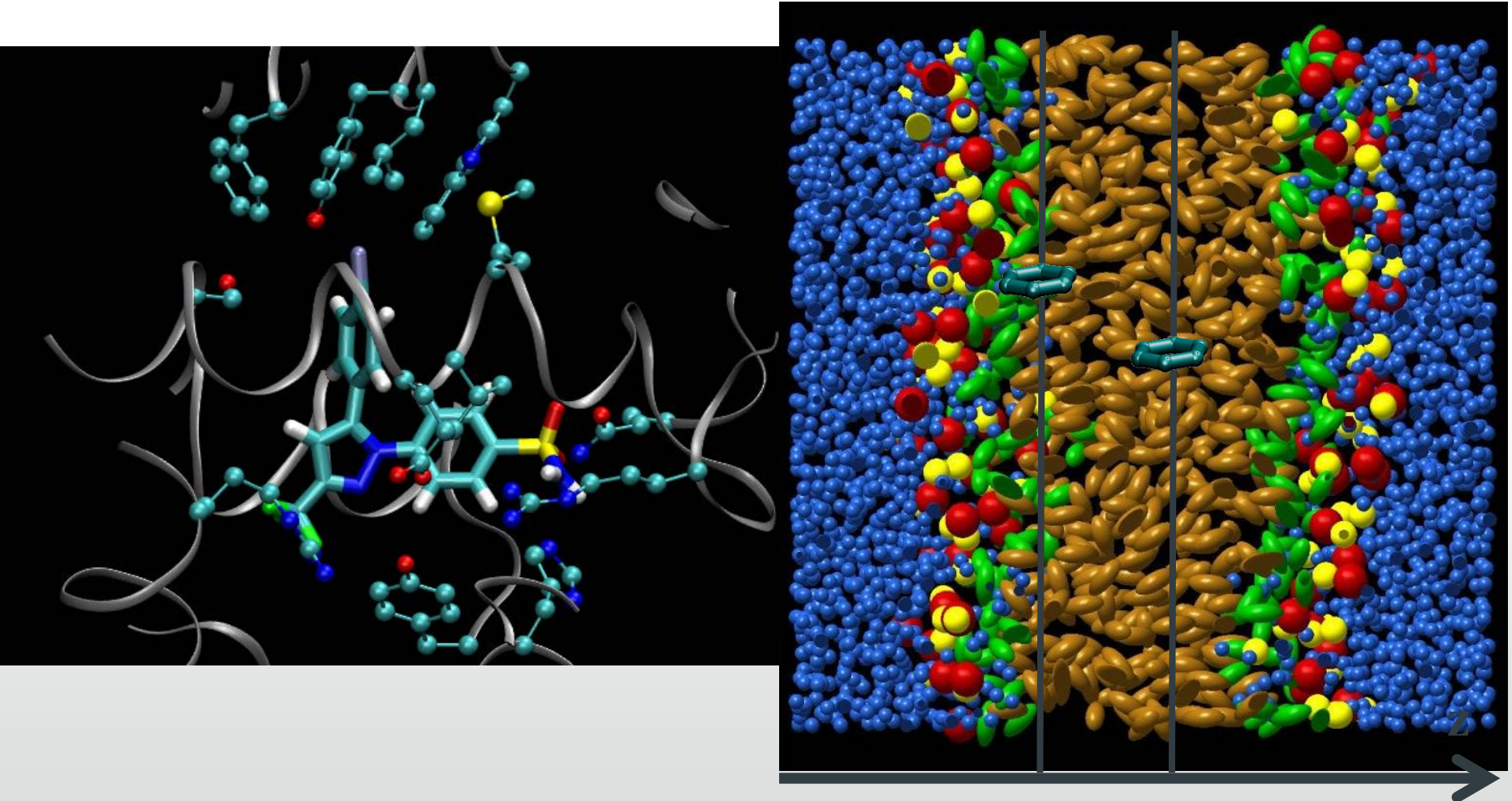


# What are our target systems?



# What do our simulations look like?

$z_I$        $z_{II}$



# Simulation techniques

There are generally two choices for molecular simulations:

- Molecular dynamics – solve Newton's equations of motion of all the atoms in the system to produce a time dependent trajectory
- Monte Carlo – select configurations of the system (at random) from the appropriate probability distribution



# Summary of simulation techniques

## *Molecular dynamics*

*Input:* potential model  
derivatives (forces)  
required

*Method:* solve Newton's  
equations

*Output:* time dependent  
trajectory

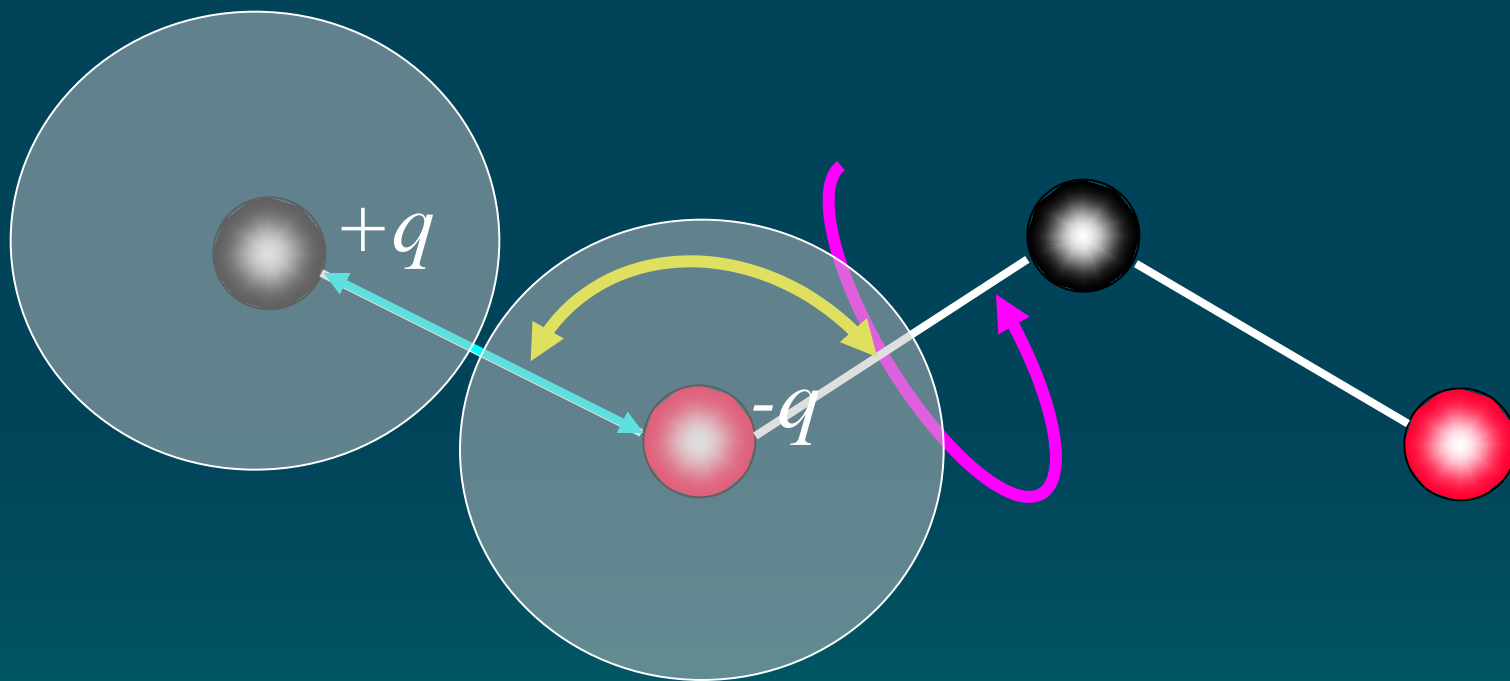
## *Monte Carlo*

*Input:* potential model  
derivatives not required

*Method:* sampling according to  
Boltzmann weight

*Output:* random trajectory

# Molecular mechanics



Molecular Mechanics: use of the potential energy

$$E_{\text{potential}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{van der Waals}} + E_{\text{coulomb}}$$



# Statistical mechanics

Some notation on vectors:

Positions of all atoms  $\mathbf{r}^N = (\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_5, \dots, \mathbf{r}_N)$

Position of one atom  $\mathbf{r}_i = (rx_i, ry_i, rz_i) = (x_i, y_i, z_i)$

Similar notion will be used for the momenta ( $\mathbf{p}^N$ )

# Statistical mechanics

N atoms at positions  $\mathbf{r}^N$  with momenta  $\mathbf{p}^N$ , the value of a property  $A(\mathbf{r}^N, \mathbf{p}^N)$

As time evolves, the positions and momenta of the atoms will change and  $A(\mathbf{r}^N, \mathbf{p}^N)$  will fluctuate around its mean value (at equilibrium)

To calculate the value of A, we can follow the system through time and average A along the path (time average):

$$\begin{aligned}\langle A \rangle &= \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t A(\mathbf{r}^N(\tau), \mathbf{p}^N(\tau)) d\tau \\ &= \frac{1}{N_{obs}} \sum_{obs} A_{obs} \quad \text{molecular dynamics}\end{aligned}$$

# Statistical mechanics

- Or... consider an infinite number of systems at a single time
- Define a probability of finding a certain configuration as  $\rho(\mathbf{r}^N, \mathbf{p}^N)$
- An ensemble average can then be defined as

$$\langle A \rangle = \int A(\mathbf{r}^N, \mathbf{p}^N) \rho(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N.$$



Probability of finding a particular state

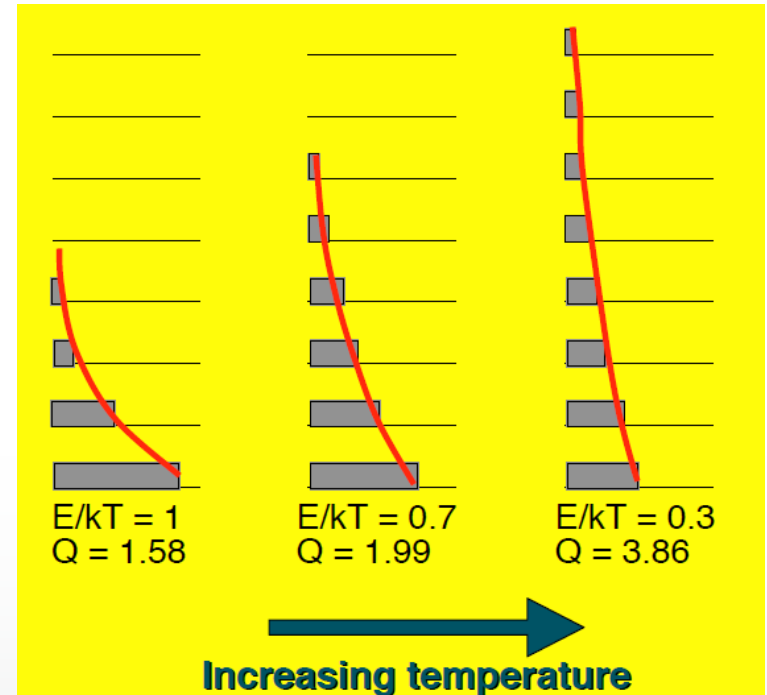
# Monte Carlo simulation

- We want to calculate:

$$\langle A \rangle = \frac{\int A(r^N) \exp(-\beta U(r^N)) d r^N}{\int \exp(-\beta U(r^N)) d r^N}$$

Boltzmann distribution

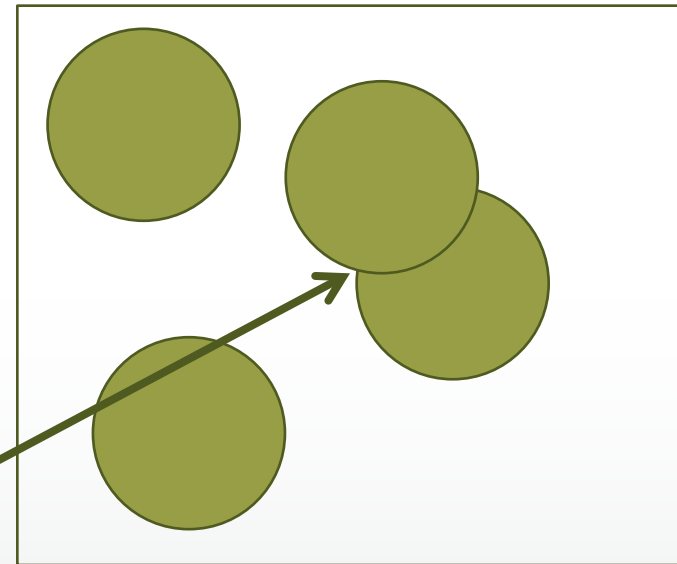
- Can we calculate these integrals for anything vaguely interesting?
- No, so we do it numerically...



# Monte Carlo simulation

- Simple Monte Carlo integration:
  - Shove the molecules in at random
  - Calculate the property we're interested in
  - Average it according to

$$\langle A \rangle = \langle A(\mathbf{r}^N, \mathbf{p}^N) \rho(\mathbf{r}^N, \mathbf{p}^N) \rangle$$



- But... most configurations have bad contacts
- $\rho$  is small, so average converges very slowly

$$\rho(\mathbf{r}^N) = \frac{\exp(-\beta U(\mathbf{r}^N))}{\int \exp(-\beta U(\mathbf{r}^N)) d\mathbf{r}^N}$$

# Monte Carlo simulation

- So we need to be clever about this...
- We need to choose states that do not have clashes, and therefore have low energies
- Rather than searching randomly, select a state according to its Boltzmann factor
- Whereas before we had

$$\langle A \rangle = \langle A(\mathbf{r}^N, \mathbf{p}^N) \rho(\mathbf{r}^N, \mathbf{p}^N) \rangle$$

- If we only generate states according to  $\rho$ , we get

$$\langle A \rangle = \langle A(\mathbf{r}^N, \mathbf{p}^N) \rangle$$

# Importance sampling

- Need to bias how we choose our configurations
- Accept our moves according to:

$$\min\{1, \exp(-\beta(U(\text{new}) - U(\text{old})))\}$$

- Choose new coordinates and calculate their energy
- Compare this energy with the old value
- If  $U(\text{new}) < U(\text{old})$ , accept the move and repeat
- If  $U(\text{new}) > U(\text{old})$ , this is uphill in energy and could be bad
- Accept move according to Boltzmann probability
- If fail, recount the old configuration and start again



# Derivation of the acceptance test

- Detailed balance condition (to ensure stable Boltzmann distribution):

$$\rho(o)\pi(o \rightarrow n) = \rho(n)\pi(n \rightarrow o)$$

- So what about the transition matrix  $\pi$ ?

$$\pi(o \rightarrow n) = \alpha(o \rightarrow n)acc(o \rightarrow n)$$

- $\alpha$  is the chance of performing the trial move  $o \rightarrow n$
- $acc(o \rightarrow n)$  is the probability of the move being accepted

# Derivation of the acceptance test

- If  $\alpha$  is symmetric:

$$\alpha(n \rightarrow o) = \alpha(o \rightarrow n)$$

- Whence:

$$\begin{aligned} \frac{\pi(o \rightarrow n)}{\pi(n \rightarrow o)} &= \frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \frac{\rho(n)}{\rho(o)} = \frac{\exp(-\beta U(n))}{\exp(-\beta U(o))} \\ &= \exp(-\beta(U(n) - U(o))) \end{aligned}$$

- Choice of Metropolis:

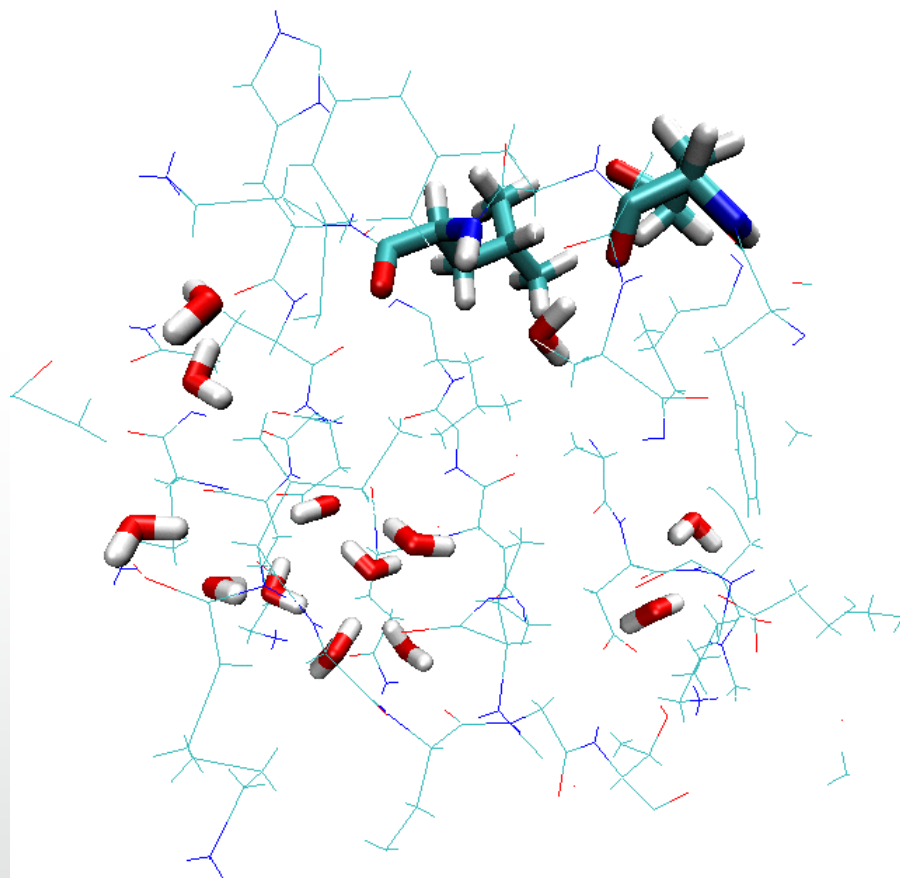
$$acc(o \rightarrow n) = \exp(-\beta(U(n) - U(o))) \text{ if } U(n) > U(o), \text{ else}$$

$$acc(o \rightarrow n) = 1$$

- Constant NVT conditions

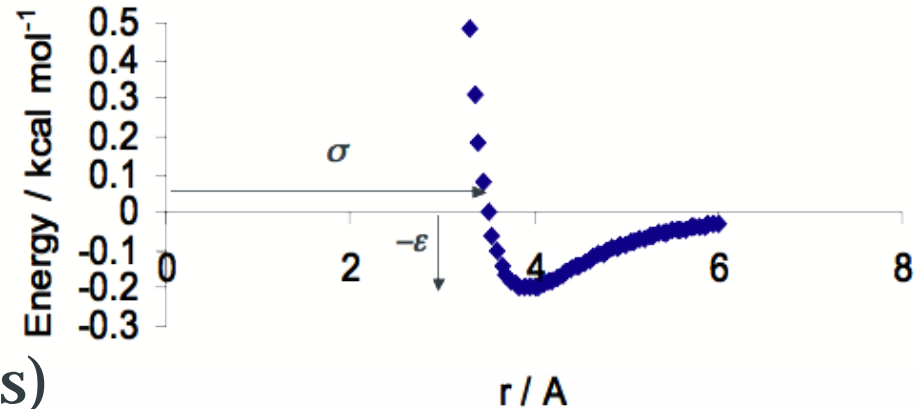
# Crazy moves!

- Grand canonical Monte Carlo –  $\mu$ VT ensemble
- Number of molecules allowed to vary
- Move involves trial insertions and deletions of whole molecules
- Avoids having to wait for molecules to diffuse by translation



# Lennard-Jones potential

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



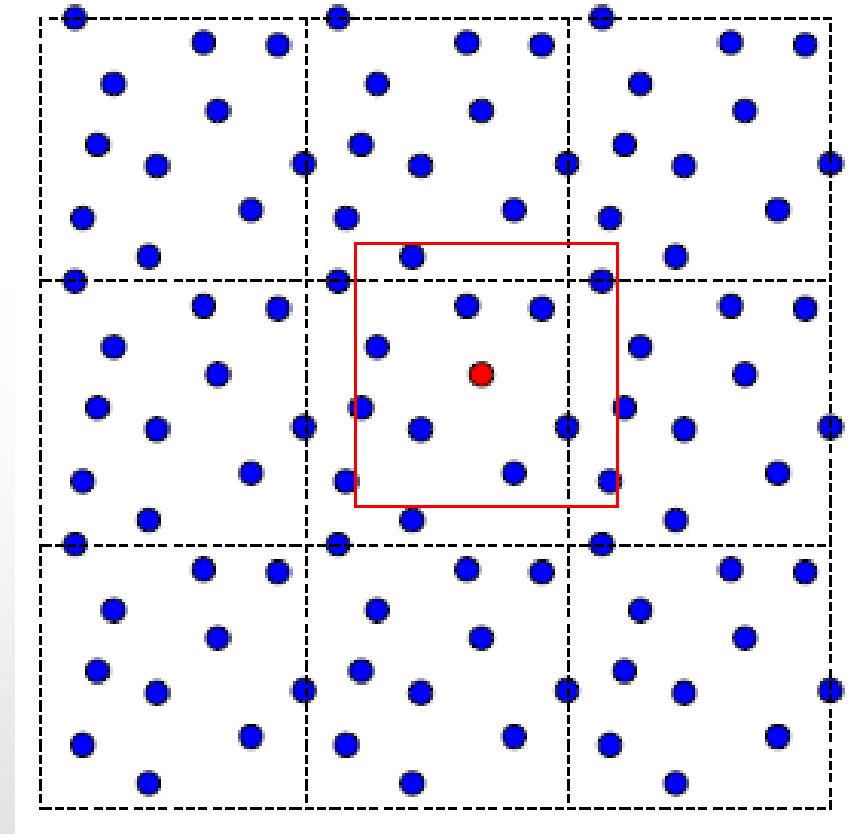
- Reduced units (dimensionless)
- $u^* = u/\varepsilon$ ,  $r^* = r/\sigma$
- $u^*(r^*) = 4 \left[ \left( \frac{1}{r^*} \right)^{12} - \left( \frac{1}{r^*} \right)^6 \right]$
- $P^* = \frac{P\sigma^3}{\varepsilon}$ ,  $\rho^* = \rho\sigma^3$ ,  $T^* = \frac{k_B T}{\varepsilon}$
- Simplifies number of available states

# Periodic boundary conditions

- To minimise simulation system size, and obtain bulk properties
- ‘Replicate’ simulation cell
- Calculate interactions with nearest image molecule

$$U = \frac{1}{2} \sum_{i,j,n} u(|r_{ij} + nL|)$$

- Truncate interactions at some cutoff less than  $L/2$  in size



# Long-range corrections

- For short-range potentials (like the Lennard-Jones)

$$U^{tot} = \sum_{i < j} u_c(r_{ij}) + \frac{N\rho}{2} \int_{r_c}^{\infty} dr u(r) 4\pi r^2$$

- For the Lennard-Jones potential:

$$u^{tail} \equiv \frac{8}{3} \pi \rho \left[ \frac{1}{3} \left( \frac{1}{r_c} \right)^9 - \left( \frac{1}{r_c} \right)^6 \right] \text{ per particle, reduced units}$$

$$p^{tail} = \frac{16}{3} \pi \rho^2 \left[ \frac{2}{3} \left( \frac{1}{r_c} \right)^9 - \left( \frac{1}{r_c} \right)^3 \right]$$

# And calculating pressure?

- From the virial thus:

$$P = \frac{\rho}{\beta} + \frac{vir}{V}, \text{ where}$$

$$vir = \frac{1}{3} \sum_i \sum_{j>i} \mathbf{f}(\mathbf{r}_{ij}) \cdot \mathbf{r}_{ij},$$

where  $\mathbf{f}_{ij}$  is the inter-particle force



# Generating trial configurations

(i) Move all atoms

(ii) Move just one atom

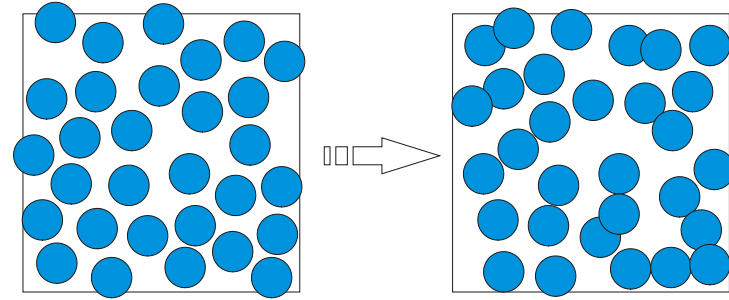
Clashes less likely than by  
random insertion

And for single particles:

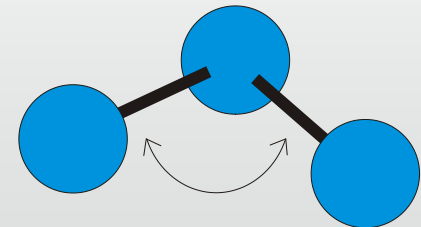
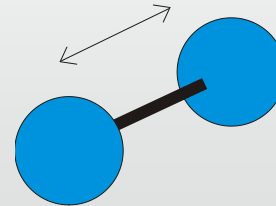
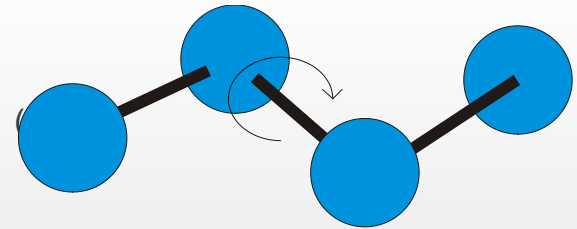
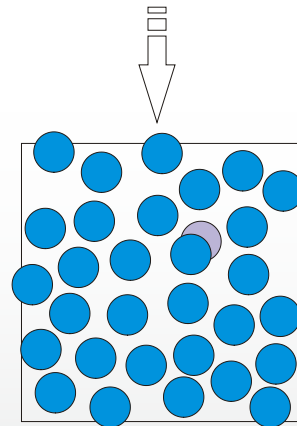
$$x'_i = x_i + \Delta(\text{Ranf} - 0.5)$$

Similarly for y and z

Choose  $\Delta$  to give acceptance rate of ca. 40%



(i)



# For next workshop...

- Write an MC code for small number (say 500) Lennard-Jones particles
- 3D periodic simulation box – PBC
- Use reduced units
- Lennard-Jones potential with truncation,  $r_c$  set to  $L/2$
- Include tail corrections for energy and pressure
- Calculate pressure for differing densities, for selected temperatures
- What happens at the lower temperatures and why?

# Summary

- Statistical mechanics
- Monte Carlo simulations
- Simple interaction potential – Lennard Jones
- Reduced units
- System properties and associated long-range corrections
- And a workshop problem for next week...