The Monte Carlo Method

The Metropolis Monte Carlo method was published in 1953 and is one of the standard methods for simulating atomic and molecular systems. Its normal use is to obtain stationary (i.e. not changing with time) thermodynamic properties as for instance energy and heat capacity. The properties can be calculated at various conditions as for instance constant energy and volume, constant temperature and volume or constant temperature and pressure.

In the following example we want to calculate the average potential energy at constant volume for liquid benzene (Fig 1).

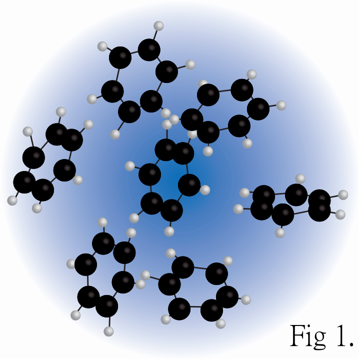


Fig 1.

By a configuration **x** we mean a vector with all the x, y and z coordinates of all the atoms in our system. For a system with 100 benzene molecules the vector **x** will therefore contain

100 molecules • 12 atoms • 3 dimensions = 3600 elements.

According to statistical thermodynamics the average potential energy of the liquid benzene system is

$$\left\langle E \right\rangle = \int \dots \int E\left(\mathbf{x}\right)\ e^{-E(\mathbf{x})/k_B T}\, d\mathbf{x} \qquad (*)$$

where $E(\mathbf{x})$ is the potential energy between the atoms for the configuration **x**, k_B is Boltzmann's constant and T is the temperature. The domain of the integral is all space available for the liquid.
The Boltzmann factor

$$e^{-E(\mathbf{x})/k_B T}$$

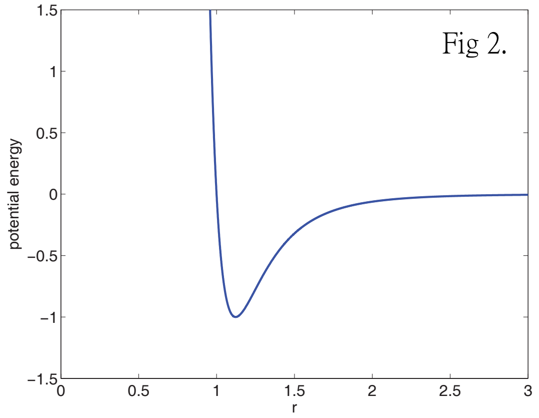
is proportional to the probability that the system is in the configuration **x**.

Already in this small system of 100 molecules we see that we need to evaluate an integral of dimension 3600. A numerical calculation of the integral by conventional methods is practically impossible. Instead we use the Monte Carlo method.

The forces and potential energy between the interacting atoms are given by a so-called force field. One common part of the force field is the Lennard-Jones energy. Two neutral atoms brought together from far apart generally attract each other due to dispersion effects. However, if they are brought too close the electron clouds start to overlap and the atoms repell each other. These two contributions are combined into the simple expression of the Lennard-Jones energy, displayed in Fig 2.

In addition, atoms with partial charges also interact electrostatically. The force field for liquid benzene also contains potential energy due to stretching, bending and torsion of convalent bonds.

In condensed systems much of the space is not available for an atom because the repulsion from neighbours is too high. Thus the Boltzmann factor take non-zero values only at limited regions in the space. In Fig 3 the Boltzmann factor is shown for a 2D condensed atomic system where the red dots indicate atoms. Hence we can conclude that in Eq. (*) the integrand is zero for many configurations **x**.



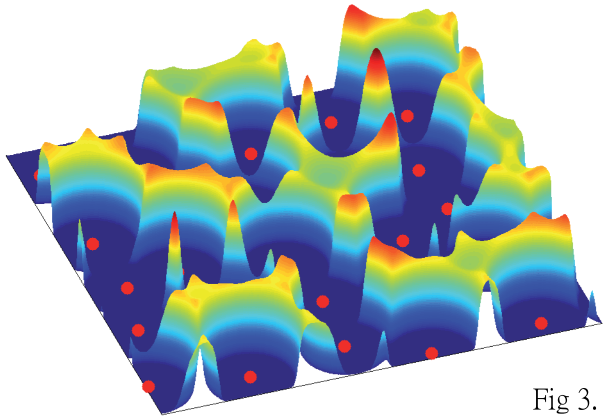


Fig 3.

In the Monte Carlo method, a high number N of configurations are randomly generated. However, the special algorithm generates configurations according to their probability

$$prob\left(x\right) \propto e^{-E(\mathbf{x})/k_B T}$$

Hence the average energy can be sampled as

$$\left\langle E \right\rangle \approx \frac{1}{N}\sum_{i=1}^{N} E\left(\mathbf{x}_i\right)$$

One way to generate configurations is to start with a lattice configuration. Then one randomly selected molecule or atom is moved a short random distance. The ratio between the probabilities for the new and old configurations are compared with a random number. If the ratio is greater than one the new configuration is always accepted, otherwise it is accepted with a probability equal to the ratio. If the new configuration is rejected the old configuration is counted once more. After that, again a new configuration is generated and so on. In the beginning of the simulation the configurations may not represent the system in equilibrium so they are not included in energy sampling.

A simulation with 100.000 atoms is demanding. Still it is a small system on a macroscopic scale. One of the issues with such a system is that the fraction of surface atoms is unrealistically high. One way to avoid surfaces despite the small system size is to use Periodic Boundary Conditions (Fig 4). Infinitely many identical copies of the (central) system are created at all sides of the central system. Thus no surfaces are present. When an atom is moved in the central system, all its copies are moved likewisely. Therefore the number of degrees of freedom has not increased.

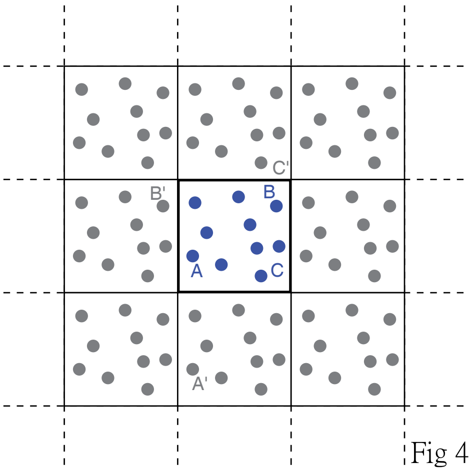


Fig 4.

Although Periodic Boundary Conditions is a smart way to avoid surfaces it has not made the system truely macroscopic. There is a periodicity in the system. In the case of a crystal that may not be a problem. But big bubbles in a liquid cannot be formed in this infinite but periodic system.