

Appendix 2.1

Random Number Generation

In any Monte - Carlo simulation, the generation of random numbers is always required. Although called random, they are actually pseudo random in that they follow a predefined periodic sequence. The usual method of generating such a sequence of numbers uniformly distributed in the range $0 < \xi < 1$ is via the recursive equation.

$$N_i = a \times N_{i-1} \text{ mod } (b) \quad \text{A3.1}$$

where mod is a function returning the remainder of N/b . The i^{th} pseudo random number, ξ_i , is then defined as

$$\xi_i = N_i / b \quad \text{A3.2}$$

Here a and b are constants suitably chosen to give statistically random and uncorrelated numbers. Usually b is taken to be 2^n where n is the computer word length, thus avoiding the necessity for the mod function as ignored overflow will perform the same task. The constant a is normally chosen to be sufficiently large, and using Fourier Analysis on such problems, it has been shown (Coveyou and MacPherson, 1967) that the binary representation of a should contain a significant number of ones, and at the same time, not a close multiple of b or \sqrt{b} . For example, the Numerical Algorithms Group (NAG) routine sets a equal to 13^{13} (Routine GO5CAF), although other values could safely be used.

Appendix 3.1

Definition of phase space and ergodic.

In a phase space the atomic positions and momenta can be thought of as coordinates in a multidimensional space, the phase density will change with time. However no, system are destroyed or created during the evolution. In a phase space region, when a trajectory passes through all the points in the phase space, then each system will eventually visit all the state points, such system is termed "ergodic".

Appendix 3.2

A very useful conclusion of thermodynamics which states the mean energy of each quadratic contribution to the total energy of a molecule is the same and equal to $1/2kT$. By 'quadratic contribution' is meant a contribution to the energy that is proportional to the square of a velocity or a position. A particle of mass m that is free to travel along an axis has a kinetic energy equal to $1/2mv^2$. According to equipartition theorem, the mean energy of a large number of molecules that are at a temperature T is $1/2kT$. For a gas of molecules free to move in three dimensions, the average kinetic energy of a molecule is $3/2kT$. The total energy per mole of such a sample is this average energy multiplied by Avogadro's constant, or $3/2 RT$ (because $R=N_A k$).

Appendix 3.3

A note on reduced (or scaled) units.

In computer simulations it is common to quote (and calculate) static and dynamic properties in dimensionless “reduced units“, normally denoted by a^* . Below is a list of the reduced quantities used in this thesis.

Time	$t^* = (\epsilon/m \sigma^2)^{1/2} t$
Distance	$r^* = r/\sigma$
Temperature	$T^* = (k_B T)/\epsilon_0$
Volume	$v^* = v/(N \sigma_0^3)$
Pressure	$p^* = p / (\epsilon_0 \sigma_0^{-3})$
Spherical cut off	$r_c^* = v^{*2/3} / 4$

There are a number of advantages with reduced units. An important one is that actual values for σ and ϵ do not need to be included in the computer program and so time is saved during the calculation of the potential energies, forces, etc. In the Gay-Berne simulations reduced unit must be used because the counterparts of σ and ϵ are not assigned definitive values.