COMPUTER ASSISTED INSTRUCTION III. SIMULATION METHODS

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ABSTRACT

A didactical program showing the main features of the Monte Carlo and molecular dynamics simulation techniques is presented. Some applications of the simulation of bidimensional fluid and solid systems are presented. The program is to be used on IBM-PC compatible micro-computers.

INTRODUCTION

One of the hardest challenges in physics and chemistry is to obtain correct and usable relationships between the intermolecular interaction potentials and equilibrium, transport and microscopic properties[1]. The usual approaches to the problem consist in using different ideas such as: densities expansions, integral equations, perturbation theories, computer simulations, etc[2]. In this paper some didactical demonstrations of the most common simulation methods are proposed. The objective of the simulation methods is to avoid or to solve numerically the many-body problem constituted by the equations of motion of the molecules in a system. As a consequence, the simulation methods are able to yield the microscopic and macroscopic properties for systems whose fundamental interactions are perfectly known. The application of the simulation methods requires the use of fast computers which are not always easily accessible. However present microcomputer facilities permit to take advantage of the new approaches in teaching chemical physics[3]. Therefore a lot of benefits can be obtained demonstrating the use of the modern computational methods in the study of the gaseous, liquid or solid phases and how the physical systems behave at the moleculat level. Nowadays two common simulation methods are the Monte Carlo[4] and molecular dynamics methods[5].

SIMULATION METHODS

In both methods, one supposes that the system to be simulated can be represented by a collection of numbers associated to different molecular properties: e.g. the molecular positions and interactions. The limited power and speed of the computers does not allow to simulate systems with more than a few hundreds of particles, located in a finite cell. The basic cell is defined by the range attributed to the position variables. In this case, the cell size and wall effects may be important sources of error. These difficulties are surmounted by using an idealized repetition of the cell in all the spatial directions[6]. In this way, every molecule has an image in each of the repeated cells. Periodic conditions are applied so that the real number of molecules and the volume of the system become infinite, the numerical density remaining constant: this is the thermodynamical limit.

Fundamentally, the description of the physical system by the Monte Carlo and molecular dynamics methods is made in different manners. Both methods have the same objective: to obtain samples of the microcanonical or canonical ensembles representing the macroscopic system. In the Monte Carlo technique, the successive positions of one molecule are searched for randomly within a maximum displacement. A position change is accepted only if some restrictive conditions are obeyed. For example, the condition to accept the motion of a hard molecule will be that no overlap occurs with other molecules. In case this condition is not obeyed the molecule is conserved in its old position. The procedure is repeated randomly or successively for all molecules. In the molecular dynamics method, the successive molecular positions are obtained by numerical integration of Newton's equations of motion. If, at time t, the position and velocity coordinates of a molecule and the total force acting on it are know, the motion equations allow one to determine its position at any later time. In both methods the complete procedure is repeated until an appropriate number of samples of the canonical states is obtained.

THE PROGRAM

Generally the simulation programs are complicated, requiring a long CPU time to be processed[7]. Neverrheless, if the objective is only to give a pictorial idea of the simulation methods, simplified versions of these programs are useful to show how they work and what the computer simulations[3] can do. However one always must remember that with simplified versions no correct data can be obtained.

The program presented here shows the basic ideas of the molecular dynamics and the Monte Carlo methods. The program can be used on IBM-PC compatible micro-computers equipped with a monochromatic screen. The simulated systems are bidimensional being constituted of disk molecules. The first step in a simulation program is to assign the initial coordinates to all molecules: the disk molecules are located at the vertices of a square lattice (40 disks) or at the vertices of a triangular lattice (48 disks), the entire system appearing on the screen. The number of disks is arbitrary and was chosen at the beginning of the program, are in the 1 to 10 range, in arbitrary units. The radius value specifies the reduced density[8] and, as a consequence, the kind of state to be simulated. For example, in a hard disks system on the triangular lattice, values of the radius up to 8.73 imply the phase to be fluid while it is solid for all radius values greater than 8.73[8]. In case the square lattice is used the limiting value is 9.42. With these disk radii, the reduced density is equal to 0.88 which is the reduced density where the fluid-solid transition occurs in hard disks systems[8].

In the molecular dynamics simulations, the initial molecular velocities must also be chosen. This is done randomly by the program, which is simplified, while the correct choise is made using the Maxwell-Boltzmann velocity distribution. The molecular interaction is described through a (6-12) Lennard-Jones like interaction potential. The energy parameter (on a 1 to 10 arbitrary scale) as well as the time used in the integration of the equation of motion can be chosen by the user. These values are combinations of the common interaction force parameters between neutral molecules , the temperature and 0.1 to 0.01 ps timesteps. The total force acting on each molecule is calculated at each time step and introduced into the motion equation together with the preceding and present position in order to obtain the next position of the molecule.

In the Monte Carlo simulations, the systems are constituted of hard disk molecules. The sucessive positions of the hard disk are obtained by random motions within a maximum displacement which is an initial option. Any new position of a molecule is accepted only if no overlap of molecules is detected (this is the hard disks model).

During the simulations, the molecules will appear on the screen in their actual positions. The trajectories (molecular dynamics simulations) or the successive positions (Monte Carlo simulations) since the beginning of the simulation are presented too. An option key allows to define the present time as zero: in this case all the earlier trajectories are forgotten. The figure shown on the screen may be frozen striking a key; the simulation will proceed striking the same key again or will be ended striking another key.

APPLICATIONS

There are many didactical applications for the demonstrations of the simulation methods such as:

a) The observation of the molecular trajectories demonstrates, for example, that in the solid state the molecules are bound to fixed positions while they are not bound in the fluid state.

b) The implication of the kind and intensity of the intermolecular interactions on the trajectories.

c) The radial distribution function: this function is the source of the calculus of the thermodynamic properties. The radial distribution function is calculated all along the simulation and, as an option, shown every 10 integration steps. Another option permits to re-initialize the radial distribution function.

d) The fusion of a solid: if the chosen disk radius is only somewhat greater than the 9.42 limiting value, in the square lattice, or 8.73, in the triangular lattice, the system presents the properties of a solid. The removal of a disk (by the use of an option key) reduces the density below the limiting value, allowing observation of the solid-fluid transition. In this case, one observes the fusion to be initiated where the disk was taken away. Afterwards the fusion propagates throughout the system, generally by preferential fusion along the reticular planes or line in a bidimensional system.

e) The defects in crysrals: if, on removal of a disk, the density remains in the solid state density range, the region where the disk was removed becomes an edge dislocation.

f) The holes in the fluid phases: the existence of holes in the fluid phase is an assumption made to explain many transport properties. During fluid simulation, when the density is close to the density of the solid, the formation of holes can be observed. If a hole is created by removal of a disk, it disappears quickly because the neighborhood becomes unstable and the hole moves throughout the system. If the density of the fluid is very much lower than the solid density, large holes and molecular clusters may also be observed.

g) The lattice vibrations in a solid phase: in solid phase simulations, the oscillations of the entire lattice can be easily observed. This phenomenon represents the propagation of the thermal phonons all along the lattice.

Most of the cited examples can be observed only when a great number of time steps is used, each time step representing more or less 10^{-15}s. This means that the properties can be observed only if a lot of configurations (obtained by a long time mean) is used.

The program can be obtained from the author.

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