Reactive Molecular Dynamics Model

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Abstract

A new model molecular dynamics is proposed, which enables to incorporate chemical reactions and molecular bond formations into the simulations. An approach of probabilistic modeling of bond formations based on the system energy data provided by ab-initio calculations is outlined. The acceleration techniques to speedup the calculations and enabling to use large molecular ensembles are discussed. Results of code validations on typical molecular distributions are provided.

1 Introduction

A common drawback of molecular dynamics (MD) simulations is their inability to describe bond formation, which is essential in modeling of chemical reactions [3, 1]. This drawback can be remedied if an MD simulation could incorporate not only the intermolecular force potentials, but also allow for the possibility of different states of molecular excitation and bonding. These effects can in principle be modeled in a probabilistic sense, if the MD simulation takes advantage of the relevant probability data from ab-initio quantum mechanical simulations or experimental results.

This study attempts to develop such a model for catalytic reaction applications. In simulations of a gaseous phase and gas-solid interactions, each molecule is advanced following the classical laws of conservation of its linear and angular momenta. At the same time a bonding probability is introduced, which determines the transition event for the two atomic species to form a molecular bond. Each new molecule of a compound specie is again treated as a rigid body subjected to Newton's laws of motion. Energy distribution among the molecules which result from molecular interactions are

also calculated in a statistical sense, with distribution probabilities determined by molecule's inertia tensor and relative bonding strengths between it's constituent atoms.

This statistical approach to interactions is advantageous to a deterministic collision calculations, because the small time scale of molecular vibrations and rotations will require excessively large computing times, and would not be entirely accurate within classical approximations.

2   Implementation

To implement this approach a Reactive Molecular Dynamics simulation code (ReMoDy) is being developed in C++ [4]. The code incorporates classes to represent atoms and molecules. The properties of atoms come from the periodic table, and molecules represent various combinations of atoms. Molecules are characterized by their, mass, momentum, as well as translational, rotational, and vibrational energies. The interaction between the molecules is carried out by means of interaction potential of Lennart-Jones type. A hardball collision is also implemented to provide a comparison.

This simple model based on classical mechanics provides the key advantage of molecular dynamics simulations over the more accurate ab-initio calculations, in that it enables simulations of larger number of molecules over the same time. Ab-initio calculations are done using various approximations to the Schroedinger equation, which is a continuum partial differential equation requiring considerable computational resources for its solution. Classical calculations on the other hand, are based on a discrete particle dynamics, for which there exist efficient integration schemes.

The main problem with calculating inter-molecular interactions is in it's quadratic dependence on the number of particles. This is because the number of all pairs of particles to be considered for interactions is on the order of $N^2/2$. However, if the interaction forces are relatively short range, as is the case with Lennart-Jones potential, then the time of execution can be significantly reduced, by introducing the interaction cutoff radius and considering only interactions between particles not farther apart than that cutoff distance. One way of implementing this approach is to use the acceleration based on segmented interaction scheme, which is commonly used in MD calculations [3, 1].

In this scheme the whole domain is subdivided into cells of the size equal or greater to the interaction cutoff radius, so that each particle can interact only with the particles located in the same or adjacent cells (shaded in the

figure), but not in the cells farther apart. As illustration in Fig.1 shows, for molecule A the interaction is considered with molecules B, C, D, E, and F, whereas molecules G, H, I are excluded from the loop.

Number of cells:

$$n = (D/d)^3 \qquad (1)$$

Number of molecules in each cell:

$$m = N/n \qquad (2)$$

Time of execution on a single processor:

$$t_{single} \sim 27nm^2/2 = 27n(N/n)^2/2 = 27N^2/(2n) = \frac{27}{2}N^2(D/d)^{-3} \qquad (3)$$

When executing in parallel on n processors:

$$t_{multi} \sim 27m^2/2 = \frac{27}{2}[N/(D/d)^3]^2 \qquad (4)$$

The cell sizes can be adjusted so as to keep the number of molecules in each cell, m constant. This can be done by selecting the cell size d according to (1) and (2):

$$d = D/(N/m)^{1/3} \qquad (5)$$

Then the execution times in a single-processor and multi-processor modes become respectively:

$$t_{single} \sim \frac{27}{2}N^2(D/d)^{-3} = \frac{27}{2}N^2(N/m)^{1/3-3} = \frac{27}{2}m^{2/3}N^{4/3} \sim N^{4/3} \qquad (6)$$

$$t_{multi} \sim 27m^2/2 = \frac{27}{2}[N/(D/d)^3]^2 = \frac{27}{2}m^2 \sim N^0 \qquad (7)$$

which shows that in a single processor mode the execution time will increase slightly worse than linear in a number of molecules, and in a multi-processor mode the time of execution will not depend on the number of molecules. However, it should be noted, that the need for inter-processor communication will weaken the last statement somewhat.
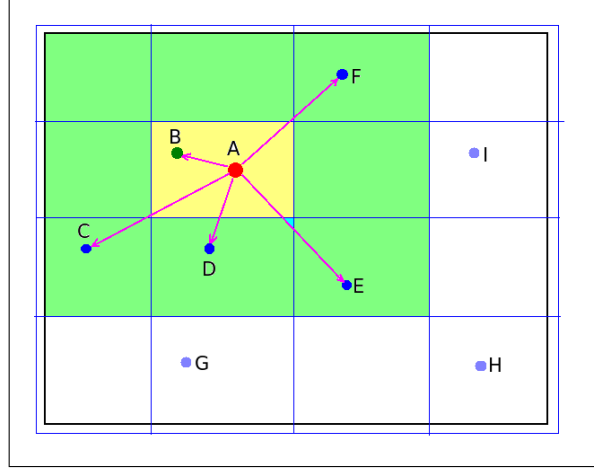
Figure 1: Segmentation of the Computational Domain

3 Results

The results of this phase of the study include the validation of the interaction mechanism for a homogeneous ensembles of particles representing a mono-atomic gas.

Figures 2(a), and 2(b) show the snapshots of ensembles of molecules for a few molecules and a large number of molecules. Fig.3 shows a comparison of velocity distribution histograms produced in simulations to Maxwell-Boltzmann distribution [2]. The study was conducted with hard-ball collision scheme for two ensembles of 10^4 molecules of helium and hydrogen.

Since the efficiency is the most important advantage factor of MD simulations, a performance test was done for different numbers of molecules. The acceleration algorithm based on segmented interaction scheme was tested on ensembles of 1000 and 10000 molecules in a single processor mode. The results were obtained on a 2GHz processor PC are presented in Tab.1, where CPU times are given for a single iteration of the algorithm which corresponds to advancement of all molecules by one physical time step. A typical relaxation time, required to transit from a low entropy to maximum entropy state of the system corresponds to approximately 100 iterations. Thus, for a system of 10^4 particles this transition can be computed in about 3 seconds of computing time. Also, as can be seen from Tab.1, considerable CPU time savings can be achieved by using the acceleration scheme which can speed up computations by a factor of 30 for 10^3 molecules and a factor of 80 for 10^4 molecules.
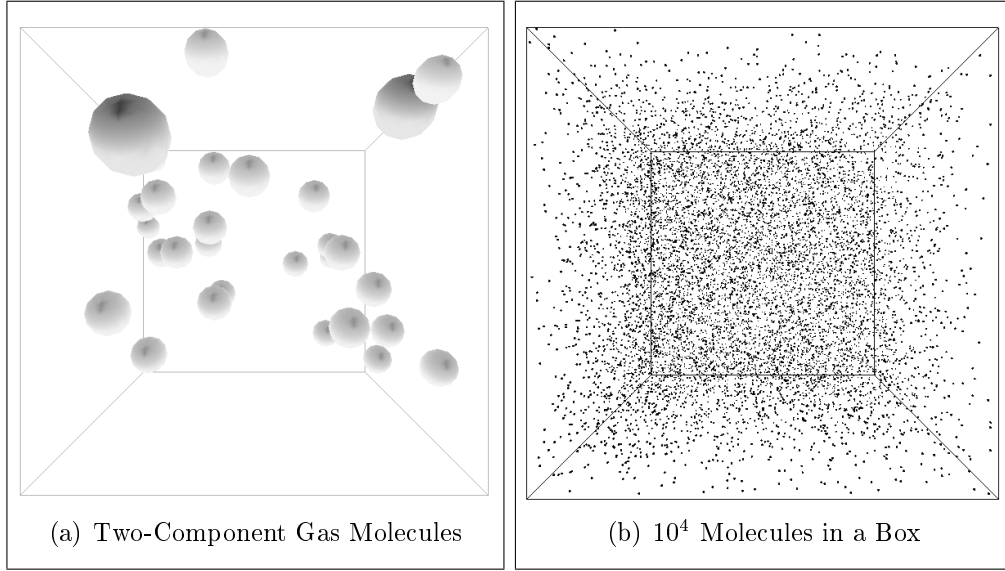
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(a) Two-Component Gas Molecules

(b) 10^4 Molecules in a Box

Figure 2: Snapshots of molecules in a box

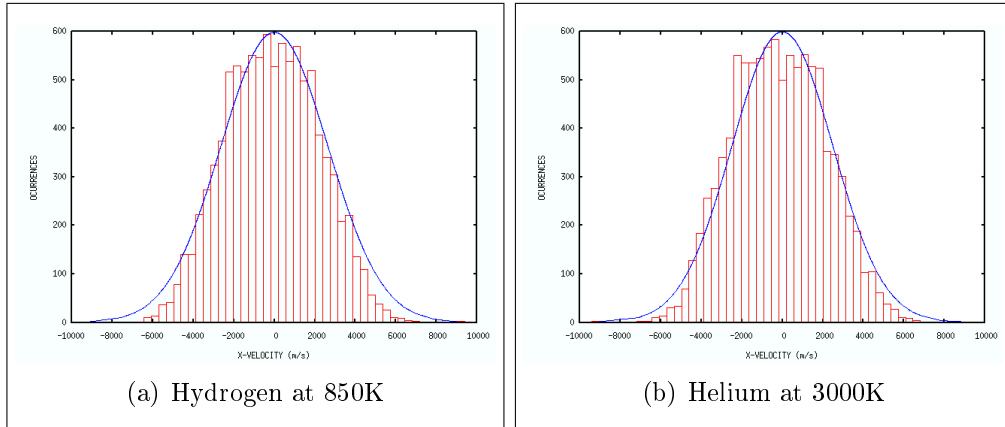(a) Hydrogen at 850K

(b) Helium at 3000K

Figure 3: Validation of Velocity Distribution

Table 1: CPU time per iteration for simple and segmented algorithms

No.molecules	CPU [10^{-3}s]	
	Simple	Segmented
10^3	80	3
10^4	2800	34

A study of different interaction potentials and diatomic gases is planned for the next step of this work.

4   Conclusions

The modeling approach pursued in this study opens opportunities for incorporating chemical bonding into molecular dynamics calculations. Efficient acceleration schemes enable computations of tens of thousands of molecules on a single workstation.

Acknowledgements

References

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