

A Coarse Graining Approach in Molecular Simulations: Fuzzy Potentials

Şebnem Eşsiz and Ersin Yurtsever

Department of Chemistry, Koç University, 34450 Rumelifeneriyolu, Sarıyer, Istanbul, Turkey

(Received 03 April 2003)

A new representation for interaction potential functions is presented. Unlike the orthodox approaches, the potential function is not a fixed function in terms of internuclear coordinates but a probabilistic one which contains information over a wide range of angular degrees of freedom. It is shown that such approaches can provide practical solutions for bulk systems of high density.

Keywords: Molecular simulation, coarse graining, interaction potentials.

1. Introduction

Molecular simulation techniques can provide a variety of new information on mesoscopic systems where the analytic theory may be too cumbersome and/or the experimental data is too difficult to obtain and analyze. With the help of the rapidly developing computer technology and the availability of professionally written software, nowadays it is possible to study the structure, dynamics and the thermodynamics of a wide range of systems such as clusters, glasses, liquids, mixtures or peptides (1).

Even though there is a large number of simulation techniques carried out over different ensembles, basically there are two approaches in studying bulk properties (1-3) Commonly used with NVT ensemble, Monte Carlo (MC) simulation consists of averaging over the configurational phase space. However, the dimensions of the phase space increases exponentially even for very small systems therefore special techniques have to be used. The standard MC simulation uses importance sampling where energetically favored configurations play more important roles in the averaging process. Although time is implicitly handled in terms of the imaginary step length, mostly the structural information is obtained from MC simulations and the time-dependent properties must be additionally derived from results.

On the other hand, the molecular dynamics (MD) simulation directly produces dynamical information in addition to the structural ones. As the implementation of the numerical integration techniques have improved, it has become the standard method of choice. An initial structure

is defined in the 6N-dimensional phase space and its time evolution is obtained from solving any set of equations of motion. Generally the Hamilton's equations may be preferable for small systems and as the number of particle increases, the Newton's equations become much more practical.

Both of these methods and any other one derived from two basic approaches rely on some sort of interparticle potential functions. They are used to calculate and compare the energy of various configurations in MC and used to calculate the time derivatives of the momenta in MD. In almost all cases, these functions either have an analytical expression or stored as numerical tables in terms of the distances between particles.

In applying simulation methods, there are serious numerical problems in high density systems. The problem lies at the great number of energetically almost degenerate minima which are connected through high barriers. As the simulations should start from a fixed -usually random- configuration, the leaving this basin and reaching another one requires large amount of energy. As a result, the simulation never becomes ergodic and the basic theorem of statistical mechanics no longer applies. In cases of such high density systems, one needs to use numerous tricks to have reasonably ergodic simulations. (4-8)

In this work, we present preliminary results from a very different approach applied to a two-dimensional system in order to overcome the high energy barriers.

2. Fuzzy Potentials

As the test case we have used a two-dimensional system of dipolar hard spheres. Each molecule

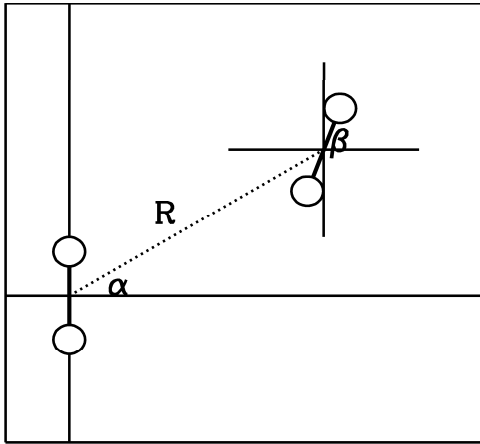


Figure 1. Coordinates defining the relative positions of two dipoles.

consists of two spheres connected by a rigid rod which then can be defined by three coordinates (x_c, y_c, ϕ) . x_c and y_c are the cartesian coordinates of the bond center and ϕ is the orientation angle. The spheres have charges of q and $-q$ so that the molecule remains neutral. Each sphere has also a Lennard-Jones center to prevent the collapse of molecules onto each other. This system in three-dimension is also known as Stockmayer fluid which shows interesting phase behavior (9-10). The interaction between two molecules (i,j) then can be written as:

$$V_{ij} = \sum c_k q^2 / r_k + 4\epsilon((\sigma/r_k)^{12} - (\sigma/r_k)^6) \quad (1)$$

Where the summation index k runs from 1 to 4 which corresponds to all pairwise interactions of $(++)$, $(+-)$, $(-+)$ and $(--)$ centers with distances of r_k . Similarly c_k is either -1 or +1 depending on whether two centers have opposite or like charges.

We have decided to use the MC simulations though the use in molecular dynamics follow in a straightforward manner. Our standard simulation consists of 338 particles placed on a square box of size 24×24 . The charge q is 0.25, and the temperature is 0.8 (all in general units). The center of masses of each particle are placed as in a layer of fcc configuration - Since the molecules are elongated in one dimension, we have used a 13×26 grid- with directional orientations being chosen

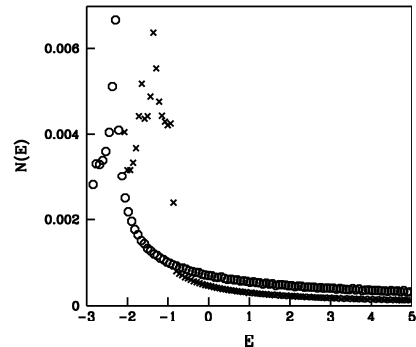


Figure 2. Number density $N(E)$ for $R=1.2$ (open circles), $R=1.5$ (crosses)

randomly.

In every step of the MC simulation, a random particle is moved randomly both by shifting the center of mass within a small area and its direction by a small amount – again randomly determined-. The energy of the new configuration is compared to the energy of the old one. If the new configuration has lower energy, then it is accepted. However, if it has a higher energy, the Boltzmann probability determines the fate of the move. In this manner, both the low energy regime is sampled more heavily and still part of the high energy regime is accessible. This procedure requires the computation of the changes in the interaction energy from Eq. 1.

If the density of the system is high, most of the dipoles are very close to each other and any attempt to separate them may shift them to the highly repulsive regions of other dipoles. To find the equilibrium structure in such cases may not be possible in reasonable simulation times. Our approach is to develop an “artificial” pathway towards the equilibrium where the energy barriers are lower than the actual ones. Once the equilibrium is reached, then using the conventional techniques one can simulate the actual system.

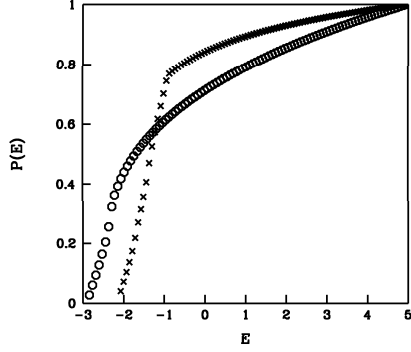


Figure 3. Probability function $P(E)$ for $R=1.2$ (open circles), $R=1.5$ (crosses)

The relative positions of two dipoles can be given in by a distance and two angles defined as in Fig. 1. The variation of the angles α and β are the main reasons of generating highly overlapping structures. However, by integrating over two angles one can generate a distance-dependent energy functional. An example of these functions are presented in Fig.2 for $R=1.2$ and 1.5 . We proceed to denote the number density of as $N(R,E)$ = number of (α, β) pairs within the vicinity of energy E . Then the probability distribution is written as:

$$\rho(R, E) = \int^E N(R, E') dE' \quad (2)$$

The variations of the total probability as a function of the energy are given in Fig. 3 for the above mentioned cases.

We would like to call this approach as the fuzzy potential since the deterministic energy concept is replaced by a “fuzzy” definition of the energy. That is, the energy of a pair of dipoles having exactly the same relative conformations may have different numerical values within the course of the simulation. In our procedure, every calculation of energy becomes a random sampling from the probability distribution (Eq. 2). The first part

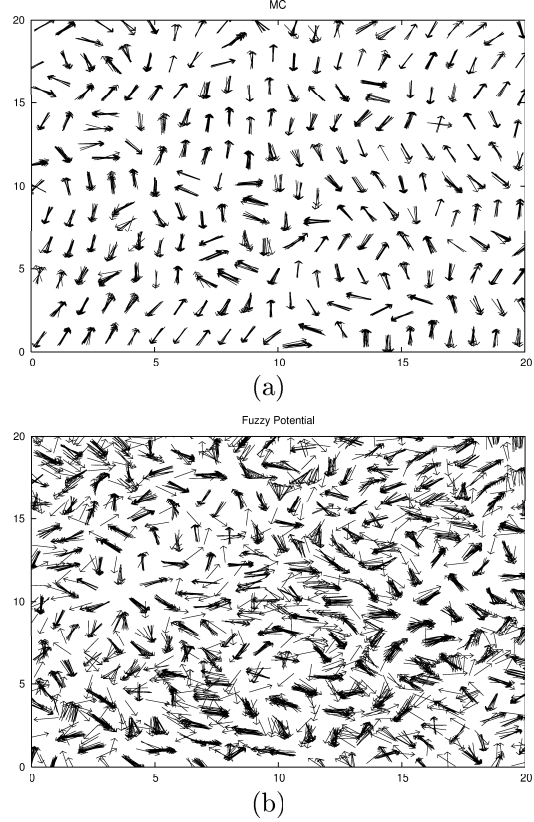


Figure 4. Superimposed snapshots from simulations. a) Monte Carlo, b) Fuzzy Potential

of the algorithm consists of a) generating an ensemble of energy values at a wide range of R , α and β , and b) computing probability distributions for fixed R values integrated over angles. Then the usual steps of MC are followed except that the calculation of interaction energy from Eq. 1 is replaced by a random sampling from Eq. 2. Since in this sampling, “hypothetically” low energy barriers are generated, a faster convergence to the equilibrium can be attained (The sampling is clearly biased towards lower energy regimes). In Fig. 4a and 4b, we compare superimposed structures obtained from MC simulations and the modified version. The MC case shows clearly that the system cannot leave its local minimum. The fuzzy potential case, though still quantitatively not good enough, shows a much improved attempt at equilibration. Similar results are obtained by analyzing the average fluctuations of

the orientational angle. During simulations with orthodox MC, the average variation of the angle is around 0.1° and it is around 1.0° for the fuzzy potential case. Clearly these numbers are very small to be very optimistic; however, this test case has an unusually high density and to get an equilibrated structure is not feasible with standard techniques.

3. Conclusions

The deterministic potential energy is replaced by a “fuzzy” probabilistic function to be used with molecular simulations. The use of the term “fuzzy” may not be the most appropriate one; however, it describes the essence of our approach. The use of the hypothetically low energy barriers allow equilibration of systems where the standard techniques fail. On the other hand, there is always the danger of reaching “unphysical” states. The optimum solution consists of alternating MC and Fuzzy potentials during the equilibration and then using MC or MD to obtain physically relevant information. The work is in progress along these lines.

References

- [1] M. P. Allen and D. J. Tildesley, Computer simulation of liquids (Oxford Science Publications, Oxford, 1989).
- [2] K. Binder, The Monte Carlo method in condensed matter physics (Springer Verlag, Berlin, 1992).
- [3] J. M. Haile, Molecular Dynamics Simulation (John Wiley, New York, 1992).
- [4] E. Yurtsever and H. Karaaslan, Ber. Bunsenges. Phys. Chem. **91**, 600 (1987).
- [5] S. F. Chekmarev and S. V. Krivov, Eur. Phys. J. **9**, 201 (1999).
- [6] Y. Levy and O. M. Becker, Phys. Rev. Lett. **81**, 1126 (1998).
- [7] K. Michaelian, A. Tamez, and I. L. Garzon, Chem. Phys. Lett. **370**, 654 (2003).
- [8] F. Calvo, J. Galindez, and F. X. Gadea, J. Phys. Chem. A **106**, 4145 (2002).
- [9] M. J. Stevens and G. S. Grest, Phys. Rev. E **51**, 5976 (1995).
- [10] S. Klapp and F. Forstmann, Phys. Rev. E **60**, 3183 (1999).