The Study of Molecule List Algorithm based on the Large Momentum Molecular System

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Abstract-- **The purpose of this paper is to propose an modified list method based on the Verlet neighbor list for the large momentum system in the molecular dynamics field. The list updated mechanism of this method is controlled by the momentum of each molecule. The variation of the list is more apparent and rapid as the system's momentum increasing through this study. Therefore, the list updated timing is realistic than the traditional Verlet neighbor list in the large momentum system, such as the nano-flow problem. It is applicable to construct the reasonable calculation and benefit to the improvement of MD's calculation.**

Index Terms-- **Molecular dynamics, Modified Verlet list, Verlet neighbor list**

I. INTRODUCTION

The algorithm is increasingly important in the analysis of molecular dynamics for the more varied topics in the micro-scale problem. The more approach to reality the problem is, the more complex the phenomena are in nano-scale. Previous studies investigated the efficient problem about MD by using various kinds of computing models. Verlet [1] published the Verlet neighbor list method to simplify the procedure of MD simulation. The displacement of each molecule is assumed as a small value in order that we just only consider the interactions in the neighborhood of each molecule. O'Connell [2] combined MD and Navier-Stokes equation to separate the shear flow field in 1995. The region near the boundary is calculated by MD, the other region is simulated by the continuous theory. Therefore, the larger system can be simulated and the CPU time will be saved. Marques et al. [3] have developed the energy particle selection method (EPS) that reduces the CPU time required in molecular dynamics simulations of ion bombardment processes. This method is based on the selective integration of the particles of the system depending on their energy. Low energy particles are integrated less frequently than the high energy ones. Glikman et al. [4] presented an optimizing molecular dynamics calculations. The method employs multiple time steps across the computational crystal both for the force evaluation and the neighbor list updating. The time step for each individual atom is chosen according to general criteria which reproduce overall accuracy while saving CPU time. In molecular dynamics simulations of systems with very hot particles in contact with a bath of cold particles one must choose a very small time step dictated by the fast particles. This requires the recalculation of all the forces after each of these small time steps. In 1996, Zhou et al. [5] showed how reference system propagator algorithms (RESPA) can be used to speed up the simulations which are that the very hot particles in contact with a bath of cold particles. Ishida et al. [6] carried out the MD of liquid water and a protein in water using several variations of symplectic integrators in 1998. The symplectic integrator is an algorithm for solving equations of motion, preserving the volume in phase space and ensuring a stable simulation. It found that the accuracy of fourth-order symplectic integrator is higher than the one of the conventional Verlet and Gear methods with the same requirements for CPU time. In 2000, Wong and Pettitt [7] presented glide-plane boundary condition (GBC) for computer simulations of interfacial systems. In addition, some researchers apply the parallel computer technology to MD algorithm. Lopez et al. [8] used coarse grain (CG) model designed to mimic the lipid molecule (dimyristoylphosphatidylcholine, DMPC) is used to study the self-assembly of a lamellar bilayer starting from a disordered configuration. Comparisons with results for an all-atom model of DMPC suggest that the CG model is about four orders of magnitude less demanding of CPU time. In addition, some researchers apply the parallel computer technology to MD algorithm. In 1994, Plimpton [9] presented three parallel algorithms, there are atom-decomposition method, force-decomposition method and spatial-decomposition method, separately. The researchers develop the parallel molecular dynamics on the basis of these algorithms later. In 1999, Schwichtenberg et al. [10] combined the fast multipole method and cell multipole method on the parallel algorithm to raise the efficiency. In 2003, Jabbarzadeh et al. [11] get an insight into the effects of molecular architecture in the behaviour of thin lubricant films to devise an algorithm for simulation of branched molecules. They have used this algorithm successfully to simulate branched isomers of C30. However the algorithm is flexible enough to be used for the simulation of more complex branched molecules. The resulting algorithm can be used in molecular dynamics simulation of branched molecules and could be helpful in designing new materials at the molecular level.

This paper will present a reasonable algorithm to avoid the too much missing of the fast molecule between the two Verlet neighbor lists in the larger momentum system. The purpose of

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this paper is to obtain the new list algorithm in the larger momentum system applicable to construct the reasonable calculation of the molecular dynamics.

II. MATHEMATICAL MODEL

The purpose of this paper is to propose an modified list method based on the Verlet neighbor list for the large momentum system in the molecular dynamics field. The lid-driven triangular cavity flow problems are examined numerically by MD with the leap-frog method [12, 13] and the modified neighbor list based on the momentum control.

A half-step scheme is used in the leap-frog method. The algorithm is formulated as follows

$$\vec{r}^*\left(t^*+\delta t^*\right)=\vec{r}^*\left(t^*\right)+\delta t^*\cdot\vec{v}^*\left(t^*+\frac{1}{2}\delta t^*\right) \tag{1}$$

$$\vec{v}^*\left(t^*+\frac{1}{2}\delta t^*\right)=\vec{v}^*\left(t^*-\frac{1}{2}\delta t^*\right)+\delta t^*\cdot\vec{a}^*\left(t^*\right) \tag{2}$$

As well, the process of generating the initial velocity of each molecule needs to be explained. The processes are listed as below.

Firstly, two uniform random variables (i.e., ξ_1 and ξ_2 on (0,1)) are generated by a multiplicative random number generator.

According to the acceptance-rejection technique [20], it can be calculated as

$$\zeta_i=1-2\xi_i,\ \zeta^2=\zeta_1^2+\zeta_2^2,\ \text{i=1,2} \tag{3}$$

when $\zeta^2 \langle\ 1$, two vector is taken as ζ_1/ζ and ζ_2/ζ

The speed of each molecule is a combination of two vectors.

$$\left(v^*\right)^2=\left(v_x^*\right)^2+\left(v_y^*\right)^2,\ v_x^*=v^*\times\frac{\zeta_1}{\zeta},v_y^*=v^*\times\frac{\zeta_2}{\zeta} \tag{4}$$

The instantaneous velocity of molecule is corrected at each time step, and the correction of molecular velocity is listed as below.

$$T_a^*=\frac{1}{3N}\left\langle\sum_i v_i^{*2}\right\rangle,\ v_i^{*,new}=v_i^*\sqrt{\frac{T_s^*}{T_a^*}} \tag{5}$$

where N is the number of molecules in the specified region, T_a^* is the instantaneous dimensionless temperature of the specified region after all of the colliding processes at each time step, T_s^* is the initial dimensionless temperature of the specified region, v_i^* is the dimensionless velocity of the i-th molecule after a colliding process at each time step ,and $v_i^{*,new}$ is the dimensionless corrected molecular velocity of the i-th molecule.

Based on the statistical thermodynamics, it is known that the initial velocities of the molecules in the equilibrium system are distributed according to the Maxwell-Boltzmann velocity distribution while the temperature of the isolated system is fixed. In the simulated equilibrium process, the molecular velocity is correlated at each time step and leads to the equilibrium state when the system is maintained to be a particular temperature. The Maxwell-Boltzmann velocity distribution means that, if the dimensionless temperature of the system is T^*, the probability of the i-th molecule having a dimensionless velocity value between v^* and v^*+dv^* is

$$P\left(v^*\right)dv^*=\sqrt{\frac{m}{2\pi k_BT^*}}\exp\left(-\frac{m}{2k_BT^*}v^{*2}\right)dv^* \tag{6}$$

In addition, the net momentum of the system must be equal to zero in order to guarantee that the system will not move due to an external force. The conservation conditions for the momentum are described as below.

$$v_i^{*,new}=v_i^*-\frac{1}{N}\sum_{i=1}^{N}p_i^* \tag{7}$$

where p_i^* is the dimensionless momentum of the i-th molecule.

The focus of the lid-driven cavity flow problem is to find the gross fluid motion instead of the instantaneous velocity. The average velocity $v_{i,k,J}^*$ of the gross fluid motion is shown as follows:

$$v_{i,k,J}^*=\left(\frac{x^*\left(i,k\right)-x^*\left(i,k-J\right)}{J\Delta t^*},\frac{y^*\left(i,k\right)-y^*\left(i,k-J\right)}{J\Delta t^*}\right) \tag{8}$$

where $\left\langle x^*\left(i,k\right),y^*\left(i,k\right)\right\rangle$ is the position of the molecule i at time $t_k^*=k\Delta t^*$, $\left\langle x^*\left(i,k-J\right),y^*\left(i,k-J\right)\right\rangle$ is the position of the molecule i at time $t_{k-J}^*=\left(k-J\right)\Delta t^*$, $J=10000$.

Verlet list assumed that the displacement of each molecule is not too large in a short time. In addition, the second cut-off radius r_v is introduced. The molecules within the radius, r_v, of molecule, i, are listed before the interaction between two molecules is calculated. Therefore, we just only consider the interaction among those molecules within the Verlet list. But, it is not easy to decide how many time steps we need to update the Verlet list in the larger momentum system. In this paper, the mechanism of the list updating is controlled by the momentum of each molecule. The modified neighbor list is updated as the number of the molecule, this displacement is larger than r_v-r_c, is larger than a critical value. In this research, the displacement, D, of each molecule (either the listed molecule or the un-listed one) will be check in each time step. In addition, $S+U$ is defined as the number of the molecule which is different with the Verlet list in each time step, where S is the number of the listed molecule which departs from the Verlet list in each time step, and U is the number of the un-listed molecule which gets into the Verlet list in each time step. As $S+U$ is larger than a critical value M_c, the modified neighbor list is updated.

III. SIMULATION DETAILS

The modified neighbor list is proposed to study the MD problem with the leap-frog method. Here, the 2-D lid-driven cavity flow problems are the test examples in this research.

Our simulations consider twelve models which have $N=656$, 1092, 1640, and 1956 water molecules, and the motion of the top plate is uniform and moves in the negative x-direction, the dimensionless velocity of the top boundary is assumed as -20, -40, and -80, respectively. In addition, an extended length is allowed, and the fluid is always enclosed by the top plate. The wall boundary condition is considered to be the position that the water is absorbed intact on the wall [14]. The initial systems of the cavity flow are shown in Fig. 1. The interaction between two water molecules is modeled by the Lennard-Jones potential.

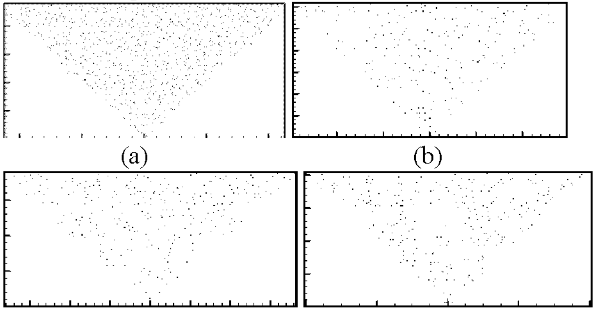

Fig. 1. The initial simulated system.((a)N=656, (b)N=1092, (c)N=1640, (d)N=1956, vector length factor=0.6)

The parameters of this simulation are listed as below.

Repulsive core ($\sigma = 2.725\mathring{A}$), parameter of energy ($\varepsilon = 4.9115\times 10^{-21}J$), and the mass of water ($m = 30.103\times 10^{-27}kg$) [15], then the dimensionless Lennard-Jones potential is

$$\varphi^*\left(r_{ij}^*\right) = 4\left[\left(\frac{1}{r_{ij}^*}\right)^{12} - \left(\frac{1}{r_{ij}^*}\right)^{6}\right] \tag{9}$$

Therefore, the dimensionless acceleration generated from the force of molecule j to molecule i is

$$\vec{a}_i^* = -\left(\frac{\partial \varphi_{ij}^*}{\partial r_{ij}^*}\right) = 24.0\times\left(\frac{2.0}{r_{ij}^{*13}} - \frac{1}{r_{ij}^{*7}}\right)\frac{\vec{r}_{ji}^{\,*}}{r_{ij}^*} \tag{10}$$

In the molecular dynamics, the truncation distance of potential must be considered. According to the research of Allen and Tildesley, the cutoff distance is $r_c = l/2$ [16] where l is the length of the model. The detail descriptions about the numerical method are described in [17].

The simulations are started by equilibrating an initially crystalline fluid for the velocity distribution is satisfied with the algorithm of Maxwell velocity distribution i.e. a similar period of equilibration with the external field switched on. In this work, the total time steps except the equilibrated process are about 2.0×10^6 with a time step ($\Delta t = 0.1fs$). According to the Schlick's study [18], the general criterion of the time interval for stability of the leap-frog method is $\Delta t = \Gamma/\pi$ for a harmonic oscillator of period, Γ. The time interval, Δt, in this paper is $0.1fs$ is much less than $6.4fs$ for $H-O-H$ bend and $3.1fs$ for $O-H$ stretch. Therefore, the time step used is small enough to ensure the numerical stability. The initial temperature and the pressure of the system and the environment is $T = 309K$ and $P = 1atm$. The parameters of this simulated model are listed in Table 1. In this research, some effects are neglected such as damping, friction and energy loss.

TABLE 1
THE PARAMETERS OF THE SIMULATED MODEL

the dimensionless velocity of top plate	-20, -40, -80
initial Temp. of the system	309K
Pressure	1 atm
the molecular number	656, 1092, 1640, 1956
simulated time	2×10^6 runs
time step Δt	0.1fs

The iterative procedures for the proposed method can be summarized as follows and shows in Fig. 2:

Step. 1: The initial position of each molecule is assigned to construct a regular triangular grid in the plane. As well, the initial velocity of each molecule is constant with a random direction through the acceptance-rejection technique. With initialization accomplished, the run itself can begin. Over a period of time-steps, the system relaxes from the assigned initial conditions and approaches equilibrium.

A. Equilibrium process

Step. 2: From (9) and (10), the acceleration of molecule, $\vec{a}_i$, is solved to represent the interaction between two water molecules.

Step. 3: Calculate the new position and velocity of each molecule from leap frog method.

Step. 4: The velocity of each molecule is correlated through (5) at every time step in order to maintain the temperature of the system.

Step. 5: If the velocity distribution is satisfied with the algorithm of Maxwell velocity distribution then the process is terminated, otherwise the computation is returned to step 2.

B. Start simulation

Step. 6: Repeat the process of step 2 to obtain the acceleration.

Step. 7: Add a dimensionless velocity to the top plate in the negtive x-direction to induce the lid-driven cavity flow.

Step. 8: Calculate the new position and velocity of each molecule from leap frog method.

Step. 9: Consider the boundary condition and the different list algorithms to correlate the position and velocity of each molecule and the calculating list.

Step. 10: In order to maintain the temperature and the momentum conservation of the system, we must correlate the velocity of each molecule through (5) and (7) at each time step.

Step. 11: Terminate the process if the computed time approaches, otherwise the computation is returned to step 6.

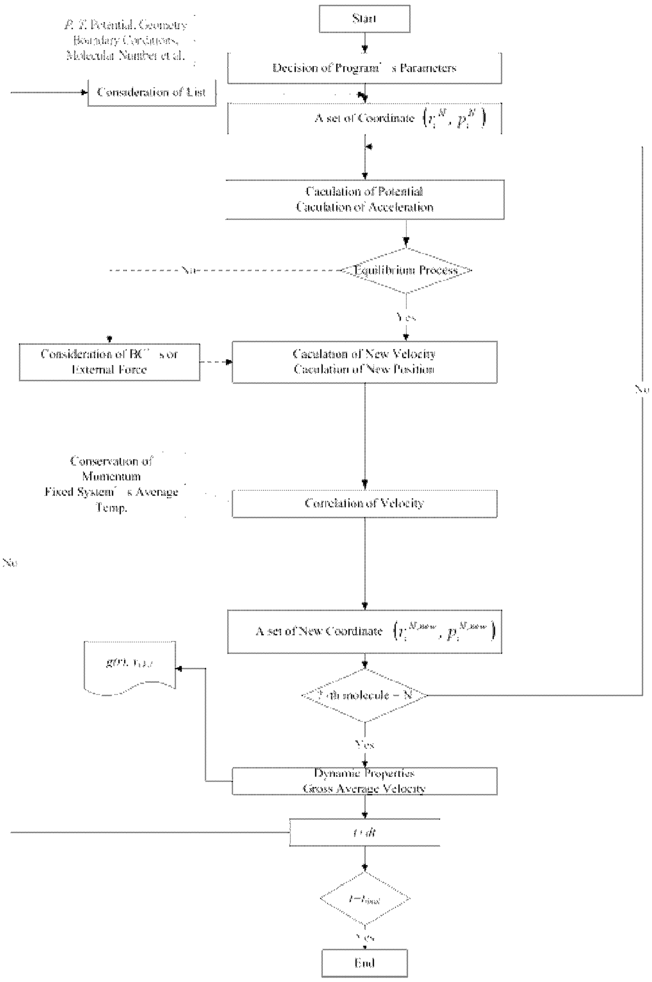

Fig. 2. The flow chart of the simulated process.

IV. RESULTS AND DISCUSSIONS

The numbers of molecule which are generated by the molecule run into or over the range of list are recorded in the various momentum systems. The average number of $S+U$ is defined as that the accumulated $S+U$ divided by the molecular number in the system along the time evolution. It represents that the quantity deviates from the original list.

The first, the effect of the molecular number in the system is observed. In Figs. 3 and 4, the average $S+U$ is shown in the different velocity of the upper plate (-20 and -40), respectively. In addition, the numbers of the molecule are 656、1092、1640 and 1956, separately. It is clear that the average $S+U$ is 140000 and 180000 as the time step is 2×10^6, separately. This represents that the effect of the number of molecule is slightly significant.

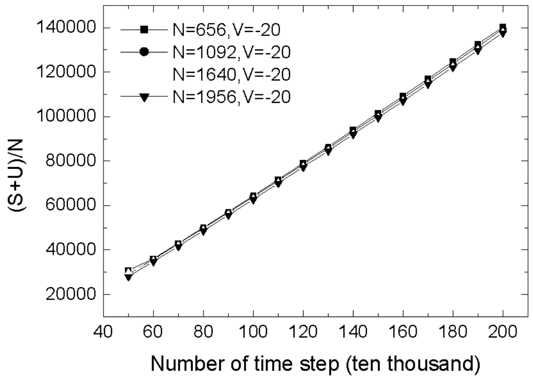

Fig. 3. The average S+U in the various molecular number as the dimensionless velocity of the top plate is -20.

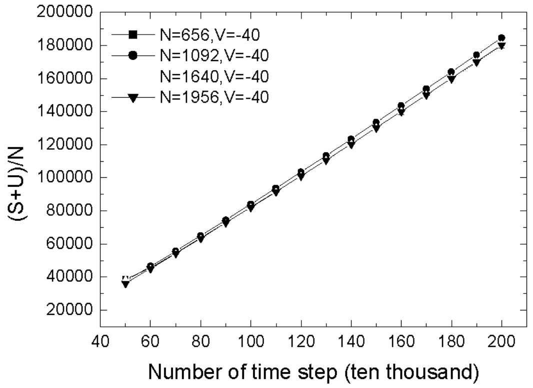

Fig. 4. The average S+U in the various molecular number as the dimensionless velocity of the top plate is -40.

In Fig. 5, the average number of $S+U$ with the various top boundary velocity (-20, -40, and -80) and the different size of the cavity (N=656, 1092, 1640, and 1956) is presented. Overall inspection of Fig. 5 discloses that the value of the average $S+U$ is 140000, 180000 and 260000 at $V=-20,-40,-80$ as the run is at 2000000 iterations. It displays that the deviation from the original list increases as the runs. In addition, the increasing of the deviation with the larger velocity is bigger the one with the smaller velocity. The deviations are similar at the same molecular number. A more detailed understanding of this relationship can be gained from Table 2 and Table 3. It represents that the opportunity of the molecule in the system departs from or gets into the range of r_v in each time step is 7% as the top plate velocity is $V=-20$, and higher to 9% at $V=-40$, 13% at $V=-80$. That is to say that the probability of the updating of list is 7%, 9% and 13% in each time step at $V=-20,-40,-80$, respectively.

TABLE 2
THE AVERAGE S+U IN THE VARIOUS BOUNDARY VELOCITY AND N = 656, 1092

Iterations(10^4)	N	656			1092		
	V	-20	-40	-80	-20	-40	-80
50		30774	38601	50249	29057	37497	48939
100		64292	82179	113111	63861	84039	116374
150		101504	130095	183639	100590	133458	187999
200		140245	179865	256908	139258	184508	261590

TABLE 3
THE AVERAGE S+U IN THE VARIOUS BOUNDARY VELOCITY AND N = 1640, 1956

iterations(10^4)	N	1640			1956		
	V	-20	-40	-80	-20	-40	-80
50		29,596	38095	50176	27964	36249	47219
100		62,815	81492	113743	62713	82064	114545
150		99,365	129862	185317	99382	130187	186655
200		137,657	180039	260118	137569	180258	261633

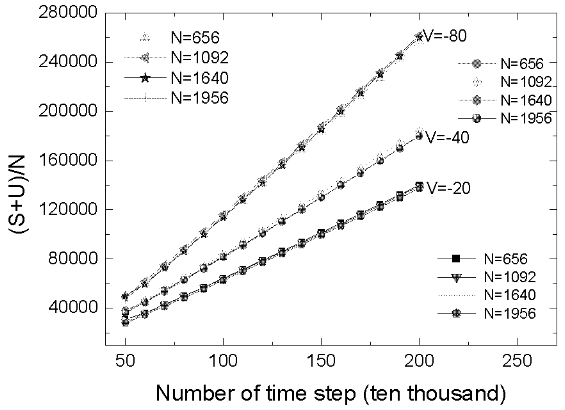

Fig. 5. The average S+U in the various boundary velocity and the different N.

Thus it can be seen that, for avoiding to simplify the problem as the Verlet list is used in the larger momentum system. We would update the list in few time steps, but loss the original meaning of the Verlet list (the CPU time saving). In addition, the gradient of the average $S+U$ will increase as the system's momentum, too. This is the reason that the number of the molecule affected by the top plate velocity increases as the run time increases. We observe that the gradient of the average $S+U$ at $V=-80$ is 1, 0.7 at $V=-40$, and 0.5 at $V=-20$. Finally, the average number of $S+U$ with the various top boundary velocity (-20, -40, and -80) at N=656 is shown in Fig. 6. The tendency is observed clearly and the updated timing is dominated by the system momentum apparently.

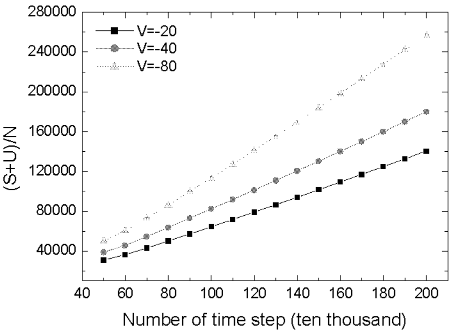

Fig. 6. The average S+U in the various boundary velocity at N=656.

V. CONCLUSIONS

For treating the larger momentum molecular system, the modified neighbor list based on the momentum control is proposed and applicable to construct the reasonable updated timing of molecular list in the MD. The 2-D lid-driven cavity flow problems are examined numerically by MD with the leap-frog method and the modified neighbor list.

Overall the above results, the number of the molecule in the system would not affect the average $S+U$. Furthermore, the opportunity of that the molecule deviates from the Verlet list is very large in the larger momentum system. In addition, the gradient of the average $S+U$ will increase as the system's momentum. According to this point, to handle the suitable list of the molecular system is the key in the molecular dynamics. Therefore, to consider the effect of the molecular velocity seriously in the larger momentum system is an important process.

These results will be benefited to the improvement of MD's calculation and the reasonable modeling of the complex system.

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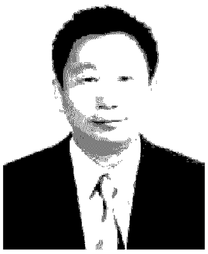
VII. BIOGRAPHIES



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