

The Molecular Dynamics Calculation of the Self-Diffusion Coefficient

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Abstract. The numerical calculation of the diffusion coefficient of liquids and gases is the subject of this paper. Moreover the problem of definition of accuracy and adequacy of such calculations is solved in the paper. To minimize errors of calculations the finite-system and finite-time corrections are constructed. The molecular dynamics method with potential of hard smooth spheres is applied in calculations. However, we used the modified algorithm of this method. As a result the method productivity has increased more than twice. For the first time, the precision calculations of the diffusion in rarefied and moderately dense gases are fulfilled.

Keywords: self-diffusion coefficient, molecular dynamics method, errors corrections, algorithm optimization.

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INTRODUCTION

The molecular dynamics (MD) method is applied today as a very powerful technique of investigation both macroscopic and microscopic properties of a wide range of media. The basic idea of this method is quite simple: the system is simulated by the set of molecules with some interaction law; their equations of motion are numerically integrated. The first paper with molecular dynamics calculations results was published fifty years ago [1]. Afterwards the MD method and its modifications were applied successfully for calculations of transport coefficients, relaxation mechanisms, phase transition and others properties and phenomena (see review [2]). The application area of gases and liquids investigations is pure media [3, 4], mixtures [5] and nanodispersed systems [6, 7].

However, we cannot say until now that the molecular dynamics method is the exact and precise calculation toolkit. There are some papers with numerical data and figures, but without exact answers to the questions about the applicability of MD method, about the values of systematical errors, caused by low molecules number in cell and finite calculations time, about the influence of the density variation on numerical results. For a long time the researches were certain that some hundreds or even some dozens molecules are sufficient for calculation of the transport coefficients, but in all results received at such a small number of molecules some empirical approximations were necessarily used. The main purpose of the present study is the solution of these problems and the formulae for minimization of methods errors definition when the self-diffusion coefficient is calculated.

Another goal of this study is modification of the method algorithm and the effective computer programs designing. It is very important because the MD computer calculations time is very large (a few weeks or months for accurate calculations).

We have used the modification of ordinary molecular dynamics method algorithm. The hard spheres law has been employed for simulation of the interaction between the fluid molecules. The modeling cell has the cubic form and contained $N = 125 \div 64 \cdot 10^3$ molecules. The density of the medium is measured by the parameter $\alpha = V / V_0$, here V is the cell volume, $V_0 = N \sigma^3 / \sqrt{2}$ is the close-packed volume of molecules, σ is the molecules diameter. The density α varies from 1.5 to 200. The periodic boundary conditions are used to compensate the finite molecules number.

Two procedures are applied for defining the molecules self-diffusion coefficient D . The first is utilization of the relation between this coefficient and the molecules velocity autocorrelation function (VACF) $\chi_{vv}(t)$ by the Green-Kubo formula

$$D = \frac{1}{3} \int_0^{\infty} dt \chi(t), \quad \chi_{vv}(t) = \left\langle \frac{1}{N} \sum_{i=1}^N \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \right\rangle, \quad (1)$$

where \mathbf{v}_i is the i -th molecule velocity.

The second way is the determination of the mean-square displacement $\langle R^2(t) \rangle = \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle$ passed by a molecule during time interval t . This characteristic is connected with the diffusion coefficient by Einstein equation

$$\langle R^2(t) \rangle = 6Dt. \quad (2)$$

OPTIMIZATION OF MOLECULAR DYNAMICS METHOD

The ordinary MD method algorithm contains the following basic steps.

1. Assignment of initial values to coordinates and velocities of molecules.
2. Calculation of the next collision time of every molecule with each other.
3. Calculation of the molecule time of the achievement of a cell boundary.
4. Choice of the minimum time value.
5. Rectilinear moving of all molecules along their trajectories.
6. Recalculation of velocities of the colliding molecules or processing of the boundary transition.

There are some modifications of the MD method (see [2] and the references cited there). One of the most effective and best-known modifications consists in splitting the modeling cell into identical zones. Such a partition allows to calculate a collision time of arbitrary two molecules on condition that these molecules are placed in the same zone. However, much computer time is spent for realization of the fifth step in this case. To minimize it we have proposed the optimization of the MD method algorithm.

Low efficiency of the fifth step of algorithm is caused by the realization of the movement of all molecules after each event (both collisions and boundary transition). It is really necessary to move all molecules, if the recalculation of collision times with all other molecules is carried out for the collided one. However, the partition of a cell allows calculating collision times in case when the pair of molecules takes place in one zone. Molecules of all other zones do not participate in this calculation, and they could be left in their places until one of the following events would occur in their zone. Such modernization has been realized and has been tested on calculations of various equilibrium and nonequilibrium properties of the system. It includes the following basic steps.

1. New variables are defined: the "individual time" of each molecule and the "current time of evolution" of the system. At the initial moment these variables are equal to zero.
2. The current time of evolution increases during the interval between the given event and previous one after each event.
3. The zone containing collided molecule or the molecules crossing some boundary is determined.
4. The number of molecules occurring in this zone is defined.
5. Each of the molecules chosen at the fourth step moves at the distance equal to the product of its velocity and the difference of the time of evolution and its individual time.
6. Only for these molecules their individual time is equalized to the time of evolution.
7. The minimal time is recalculated only for chosen molecules.
8. For the other molecules the minimal time decreases by the difference of the time of evolution and their individual time.
9. The smallest of the minimal time of all molecules is defined and the corresponding event is realized.

The given modification increases the productivity of the algorithm $2 \div 2.5$ times when the number of particles is equal to $3 \cdot 10^3 \div 3 \cdot 10^4$ and the density interval is $\alpha = 1.5 \div 20$. The area of applicability of the realized modernization of the method does not differ from the area of applicability of the initial algorithm. However, it is necessary to be punctual when the calculation of the characteristics defined by the molecules coordinates is carried

out. It is necessary to move all particles to their real position exactly before the starting point of such a calculation. It concerns calculations of pressure, mean-square displacement and other characteristics.

RESULTS OF CALCULATIONS

Let us consider the results of calculation of the self-diffusion coefficient in fluids. This calculation is difficult in liquid. It is caused by the fact that VACF relaxation has an exponential character only in rarefied gases. The dashed line on Fig. 1, plotted in the logarithmic scale, corresponds to such a relaxation. But we can show another situation in dense gases and liquids. There are so-called “long-time tails” of correlation function with a slow relaxation character, here $\chi_{vv}(t) \sim t^{-3/2}$. For the first time this behaviour of VACF was observed by Alder and Wainwright [1], later it was described by the mode-coupling theory [8]. In the earlier investigations the calculations time was small enough. For this reason the “long-time tails” were detected only in very dense media ($\alpha \leq 5$). To study the long-time tails of VACF it is necessary to calculate the later with very high accuracy. Such calculations have been carried out in present paper. The results are presented in Fig. 1. The solid line corresponds to the density $\alpha = 2$ and the dotted line corresponds to the density $\alpha = 10$. It is shown that the long-time tail begins in the case $\alpha = 10$ with the values approximately on the order smaller, than for $\alpha = 2$. The physical reason of this fact is clear. With the density increase the relaxation time grows quickly and the exponential part of VACF evolution dominate here.

Exact molecular dynamics calculations with a large molecules number and sufficient time of calculations allow to propose an accurate formula which describes VACF relaxation in dense gases and liquids

$$\chi_{vv}(0, t) = \langle \mathbf{v}^2(t) \rangle = \left[\exp(-t/\tau(\alpha)) + B(t - t_*)^{-\frac{3}{2}} \right]. \quad (3)$$

Introduced here parameters B and t_* are defined by the correlations $B = 1.245 \exp(-0.419\alpha)$, $t_* = 3.2 \ln(\alpha - 1) + 0.5$ (see also Table 1).

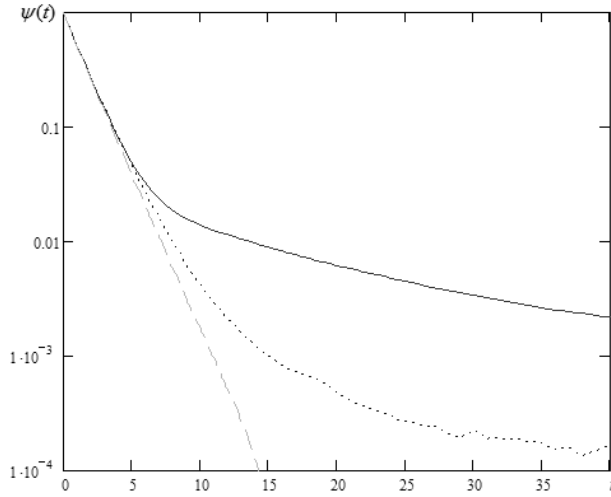


FIGURE 1. The velocity autocorrelation functions for various densities of the system. The solid line corresponds to $\alpha = 2$, the dotted line – $\alpha = 10$, the dashed line – $\alpha = 100$. The time measurement unit is the molecules mean free path time.

TABLE 1. Parameters of approximation (3). The time t in the third row defines the time interval when the approximation is valid (with accuracy δ).

α	2	3	5	10
t_*	0.48	2.87	4.91	7.54
B	0.54	0.37	0.132	0.021
t	$> 20\tau$	$> 12\tau$	$> 12\tau$	$> 12\tau$
δ	$\leq 1\%$	$\leq 2\%$	$\leq 4\%$	$\leq 6\%$

The relaxation time depends on the density as follows

$$\tau_r(\alpha) = 0.2628\alpha - 0.4328. \quad (4)$$

when the density factor $\alpha \geq 10$. Having approximations (3), (4) it is possible to obtain the values of the diffusion coefficient, they are in good agreement with the experimental results.

For the first time exact calculations of the self-diffusion coefficients of rarefied gases have been carried out. Earlier there was an opinion, that the MD method cannot be applied to such calculations, because the mean free path is about the modeling cell size in the rarefied system. However, the VACF should be defined for the time greater than the mean free path time. Despite this fact we have executed calculations of such systems and have proved that they are correct. When we use about ten thousand molecules in the cell, the results of calculations agree quite well with the Boltzmann theory and with the argon self-diffusion experimental values [9]. The additional increase of this molecules quantity does not influence self-diffusion results. The density factor α dependence of the self-diffusion coefficient has the linear character in rarefied gases (see Fig. 2).

Speaking about the opportunity of the MD method to calculate the result with the definite accuracy, it is necessary to note that it is possible if the "plateau" values consist, i.e. values of the self-diffusion coefficient when it does not depend on time. As an example the "plateau" values are reached only if $t \sim 400\tau$ when the density parameter $\alpha = 2$. The difference between the self-diffusion coefficients calculated at $t=100\tau$ and at $t=350\tau$ makes about 3% (27000 molecules were used in this calculation) [10].

The dependence of the self-diffusion coefficient on the molecules number has also been investigated. The formula which allows to connect the diffusion coefficient of the infinite system D_∞ with the coefficient D estimated in the N – molecules system has been constructed

$$D = D_\infty [1 - d(\alpha)N^{-1}]. \quad (5)$$

We should note that Eq. 5 describes the diffusion coefficient more precisely than the approximations obtained by different authors [3, 11] earlier. In particular the parameters D_∞ and d of this correlation are the functions of the medium density (see Table 2).

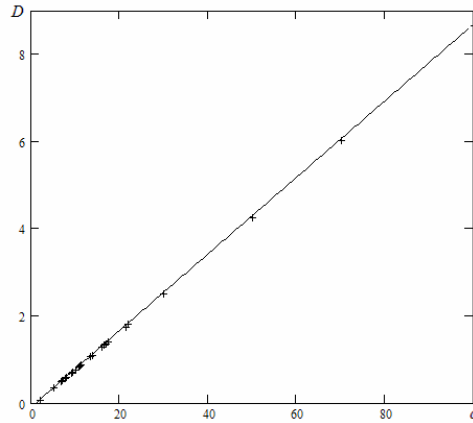


FIGURE 2. The density dependence of the diffusion coefficient, $N=27000$. The labels correspond to the calculations results, the solid line is the result approximation.

TABLE 2. The density dependence of the parameters of approximation (5).

α	2	5	10	70
D_∞	0.118	0.662	1.52	12.04
d	6.548	5.92	3.83	1.35

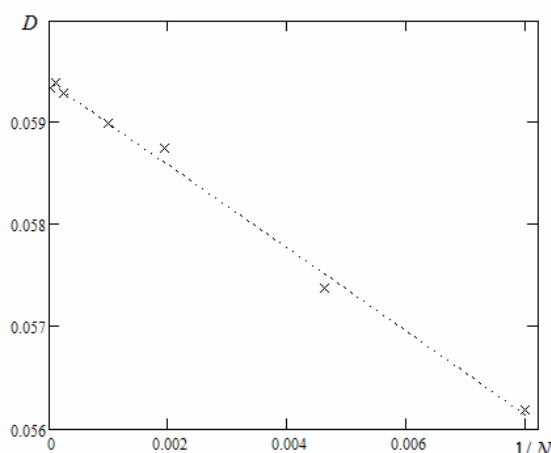


FIGURE 3. The molecules number dependence of the diffusion coefficient. The cross labels correspond to the calculations results, the dotted line is the result approximation.

The statistical errors behaviour of MD method is shown to be standard character, i.e. these errors are inversely proportional to a square root from measurements number.

Using the mean-square displacement procedure we have received almost the same numerical values. However, the next equation

$$\langle R^2(t) \rangle = 6Dt(1 - 4Bt^{-1/2}). \quad (6)$$

is proved to be more correct than Eq. 2 when the condensed system is investigated (see paper [10]).

CONCLUSIONS

The main results of this work are enumerated below.

- For the first time the precision calculations of the diffusion in moderately dense gases are fulfilled. The system with about ten thousand molecules allows to define the diffusion coefficient with the accuracy of about one percent in spite of the fact that the mean free path time is comparable to the size of the modeling system.
- The suggestion about the impossibility of the molecular dynamics method application for investigation of rarefied gases is proved to be not valid. The diffusion coefficient results are found to be in good agreement with Boltzmann values.
- All sources of calculations errors are analyzed. For the minimization of these errors the finite-system and finite-time corrections are constructed (correlations (3) and (5)).
- The calculated diffusion coefficients are shown to be in good agreement with the experimental data of the argon self-diffusion at pressure from atmosphere pressure to 30 MPa.
- The presented modification of molecular dynamics algorithm is proposed and realized in the computer programs. The modified programs allow to calculate all required physical properties in the factor of $2 \div 2.5$ faster when the molecules number exceeds one thousand.

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