Stochastic simulation of transport processes in liquids

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Abstract. The subject of this paper is molecular stochastic modeling the transport processes in liquids. The proposed method and the corresponding algorithm are an alternative to the molecular dynamics method. However, unlike the latter the system of Newtonian equations is not solved for modeling the phase trajectories of the system studied. The phase trajectories of the molecular system are simulated stochastically. For this purpose, the database of the intermolecular forces acting on each molecule of the system during the considered time interval has been created. The distribution function of these forces has been built. It was shown that this distribution function can be approximated by certain analytic function. The dependency of the parameters of this function on the liquid temperature and parameters of the intermolecular interaction potential (the Lennard-Jones interaction potential is used) is determined. Using this distribution function the force acting on each molecule at given time is determined. After that the coordinates and velocity of all molecules of the system are calculated. As a result, the full information about the phase variables of the molecular system is obtained. All macroscopic characteristics of the system (temperature, pressure, transport coefficients etc.) are calculated by means of the methods of nonequilibrium statistical mechanics. The transport coefficients are calculated using fluctuation-dissipation theorems that relate transport coefficients to the evolution of the corresponding correlation functions. The algorithm was tested on the calculation of the viscosity of several simple liquids.

1. Introduction
The molecular modeling is a single alternative to the experimental determination of the transport coefficients of liquid and gases. Practically the molecular dynamics (MD) method is the only consistent method for such modeling. The high computing resource consumption is an obvious disadvantage of this method. Given method is not applied to simulation of the rarefied gases for this reason. There is a less obvious drawback. The MD method of the simulation of the transport processes in gases and liquids does not reproduce the true phase trajectories of the simulated system (see for example [1–3]). This is due, on the one hand, to the local instability of the calculated trajectories with respect to small disturbances, and mixing, on the other. Method MD gives adequate calculation data (pressure, temperature, viscosity, etc.) by means of the averaging the corresponding dynamical variables over large number of the independent phase trajectories. As a result, MD simulation is a very computer-intensive process.

In this connection, the idea of creating an algorithm in which the phase trajectories of the considered molecular system would not have been calculated deterministically appeared there. It is clear that such trajectories should be constructed reasonably enough, taking into account the real
mechanisms of the transport processes in gases and liquids. Such stochastic algorithm to model transport coefficients of the rarefied gases has been constructed in our papers [4–6]. However, the method of stochastic molecular modeling (SMM) developed there is applicable only for the molecular systems with pair collisions only. That is why it is a rarefied gas. This method can be used to simulate the transport processes in dense gases of hard spheres where only pair collisions of molecules take place also (the so-called Enskog gas [7]). Method SMM for Enskog gas has been developed in paper [8].

In liquids the transport mechanisms are much more complicated. Strictly speaking, the transport processes in liquids are not reduced to simple molecular transfer as in rarefied gas or to superposition of molecular transfer over free paths length and molecule size as in Enskog gas. The simple estimates show that in liquids of the neutral molecules with short-range potentials in sphere of interaction of given molecule there are about a dozen molecules. In liquids the interactions of the molecules are always multiparticle ones. The aim of the present paper is to develop the ideas of the works [4–6] for the liquids. In fact a certain palliative of MD and CMM methods is offered.

2. Database of the intermolecular forces

The starting point of molecular modeling is to study the dynamics of the considered system. In the MD method to obtain the systematic information about the phase variables of the system (velocities $v_i$ and coordinates $r_i$ of all molecules) the system of Newton equations is solved

$$m \frac{dv_i(t)}{dt} = \sum_{j \neq i} F_{ij}(t) = F_i(t), \quad \frac{dr_i(t)}{dt} = v_i(t), \quad i = 1, 2, ..., N,$$

where $m$ is the mass of the molecule, $N$ is the number of the molecules in the system, $F_i$ – intermolecular forces.

Therefore, the complexity of the realisation of MD method is conditioned by two circumstances. On the one hand, we have to find the resultant force of all $N$ forces acting on each molecule in each time step. Strictly speaking to do this, we have to perform $N^2$ operations. On the other hand, further it is necessary to solve the system of Eq. (1). It is clear that in both cases there are the errors. As a result, at each time step the system jumps from a constant energy hypersurface to another, whereas the evolution of the original Newtonian system (1) in the phase space always occurs at predetermined and well-defined hypersurface. The situation would become much simpler if we have the possibility to set the force acting on molecule $i$ in every time step using some a-priory information. The starting point for building such tool is the hypothesis of some universality of the average forces acting on each molecule. This hypothesis seems reasonable because such interactions are multiparticle. Of course, this force will depend on the type of liquid, that is, on the parameters of the intermolecular potential and temperature.

To set the force acting on each molecule at given time it is necessary to have an appropriate database. In present paper such database has been created by the MD method. For this aim some molecular system with liquid density was systematically simulated. The intermolecular interactions were given by Lennard-Jones potential

$$U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right],$$

whose parameters varied widely. Here $\sigma$ is the effective radius of the molecule, $\varepsilon$ is the maximum value of the attraction energy.

During the simulation all values of the forces acting on each molecule at successive time are saved to database file. Thus, the volume of this database is proportional to the number of molecules used and time of simulation (the numbers of time steps). Using obtained values of these forces the corresponding distribution function is built. The example of the distribution function $P$ of the
intermolecular forces is presented in Fig. 1. Here, solid line corresponds to the liquid argon at temperature of 87 K. Dimensionless force in Figure is equal to $F_i = F_i \cdot 1.984 \cdot 10^{-13}$. The distribution function is built with 0.00344 steps in the range from −10 to 10. This distribution function describes the intermolecular forces of the system of 64000 molecules. The parameters of the interaction potential for the argon molecules were as follows: $\sigma = 3.405 \ \text{Å}$ and $\varepsilon/\kappa_B = 119.8 \ \text{K}$ [9] ($\kappa_B$ is the Boltzmann constant). The distribution function obtained at all temperatures is described by the function $P = \frac{1}{2} \left[ \tanh(aF_i) + 1 \right]$ with good accuracy (about 3%). The approximation of the distribution function by hyperbolic tangent at temperature of 87 K was shown by the dotted line. It is clear that the distribution function will depend on the temperature of liquid. In Fig. 1, the dots and dash lines correspond to the temperature of 43.5 and 174 K, respectively.

![Figure 1. The distribution function of the intermolecular forces of the liquid argon (solid line), dots and dash lines correspond to the temperature of 43.5 and 174 K, respectively](image)

3. Simulation algorithm

At initial time simulated liquid molecules are placed in a simulation cell which is a rectangular parallelepiped (cube) of volume $V$. The molecules are uniformly distributed in this cell with given density $n$, and the velocities are distributed according to Maxwell law at given temperature $T$:

$$f(v) = 4\pi v^2 \left( \frac{m}{2\pi RT} \right)^{3/2} \exp \left( -\frac{mv^2}{2RT} \right). \quad (3)$$

here $R$ is the gas constant and $v$ is the velocity of the molecule.

Transport processes in the volume are modeled using periodic boundary conditions. In this case, if a molecule with velocity $v_i$ leaves through one face of the simulated cell, a molecule with the same momentum enters the cell through the opposite face. As a result, along with the basic cell, the evolution of all its surrounding copies is considered. As an equilibrium state is modeled, the initial state of the system must be prepared so that the total momentum of its molecules is equal to zero and the energy corresponds to the given temperature. This was done in the same way as in [4, 5].

The algorithm is constructed traditionally. Simulation of the liquid dynamics starts with generating a list of the phase variables of the molecules at the initial time $t$. Molecules are introduced in the list in a random order. Changing the order of the particles in the list, we will obtain different phase trajectories (this, of course, is not the only method for obtaining them). Thus, at time $t$, the molecules have the following coordinates and velocities $r_1, v_1, r_2, v_2, \ldots, r_N, v_N$. It is necessary to obtain the values
of the molecules velocities at successive times in the simulation interval \((t, t_\text{s})\). We select the time interval \(\tau_1 = d/v_{\text{max}}(t)\), where \(v_{\text{max}}\) is the maximum magnitude of the velocity of the molecules in the system at the given time and \(d\) is the characteristic length of the studied system. In particular, \(d\) can be chosen equal to \(\sigma\) (see Eq. (2)). The generation of the list for the time \((t + \tau_1)\) starts with a consideration of molecule 1. We must consider that at time \((t + \tau_1)\) all coordinates and velocities should be changed. To implement the appropriate procedure, splitting dynamics into processes is used. First, the coordinate of the molecule 1 is changed, \(\mathbf{r}_1(t + \tau_1) = \mathbf{r}_1(t) + \mathbf{v}_1(t)\tau_1\), and then its velocity is determined. Using the forces distribution function, the force acting on molecule 1 at time \(t\) is determined and then its velocity is changed: \(\mathbf{v}_1(t + \tau_1) = \mathbf{v}_1(t) + \mathbf{F}(t)\tau_1\).

The generation of the list for the time \((t + \tau_1)\) starts with a consideration of molecule 1 and ends with molecule \(N\). As a result, a new list of molecular velocities and coordinates \(\mathbf{r}_1(t + \tau_1), \mathbf{v}_1(t + \tau_1), ..., \mathbf{r}_N(t + \tau_1), \mathbf{v}_N(t + \tau_1)\) is generated. After the generation of the list for the time \((t + \tau_1)\), the next time interval is selected as \(\tau_2 = d/v_{\text{max}}(t)\), where \(v_{\text{max}}\) is the maximum magnitude of the velocity of the molecules of the system at time \((t + \tau_1)\) and the procedure is repeated. This procedure is repeated until the given simulation time \(t_\text{s}\) equal to \(t_\text{s} = \tau_1 + \tau_2 + \tau_3 + \ldots + \tau_N\) is reached. The calculation result is the full set of the phase variables of all molecules of the simulated system at successive times. The conservation laws are not fulfilled in general case because the evolution of the system is determined stochastically in each time step. To eliminate this drawback, some procedure is used. This procedure is similar to the thermostats used usually in the MD method [10]. The correction of the impulse and energy was performed every 30 steps. The average energy and impulse fluctuations in the system did not exceed 0.5%.

Using nonequilibrium statistical mechanics [11, 12] and obtained information about phase variables of the studied system we can calculate all its macroscopic characteristics (temperature, pressure, transport coefficients etc.). The transport coefficients are calculated using fluctuation-dissipation theorems that relate transport coefficients to the evolution of the corresponding correlation functions. In the literature, these relations are called the Green-Kubo formulas.

In present paper the applicability of the described algorithm is studied on the example of calculating the viscosity coefficient of liquid argon at temperature of 87 K. Shear viscosity coefficient \(\eta\) was calculated from the Green–Kubo formula

\[
\eta = \frac{V}{3k_BT}\tau \left[ J_{xy}(t)J_{xy}(t + t_1) + J_{yx}(t)J_{yx}(t + t_1) + J_{xx}(t)J_{xx}(t + t_1) \right] dt_1 ,
\]

where the \(J_{xy}\) component of the stress tensor has the following form

\[
J_{xy} = \frac{1}{V} \left[ \sum_{i=1}^{N} m_i x_i y_j + \frac{1}{2} \sum_{i<j}^{N} F_{xij} y_j \right].
\]

Here \(\tau\) is the time to reach a plateau value [13], \(F\) is the force acting on a molecule, \(x\) and \(y\) are the coordinates of the molecule, and \(N\) is the number of the molecules. The angular brackets in (4) denote an ensemble average.

The simulation data obtained by the use of the described SMM method is shown in Fig. 2 (dotted line). These data are compared with the MD calculations (solid line). MD simulation was carried out by means of the package Lammps. In calculations, 64000 molecules were used. The data were averaged in both methods (MD and SMM) along 1000 independent phase trajectories. The plateau
value is reached beginning from $t = 1600$ ps. The agreement between the SMM and MD data is good, these data are consistent with accuracy of about 2%.

The MD calculations were performed on 10 processors; the calculation time on one processor was 18 hours. The calculation time of the viscosity coefficient by the SMM method developed in this work turned out to be more than an order of magnitude less. It should be borne in mind that the Lammps package has been well optimized, while the algorithm developed here has not been optimized.

Figure 2. The evolution of the viscosity coefficient (4). Solid and dotted lines obtained by the MD and SMM method, respectively.

Conclusion
The stochastic algorithm of molecular modelling of the transport processes in liquids proposed in this paper is quite simple. The performed test calculations, one of the examples of which is discussed in previous section, show that accuracy of the simulation is comparable with the accuracy of the MD method. However, the SMM method is much more economical one.

Of course, preliminary information on intermolecular forces is necessary for the implementation of the SMM method. The creation of the corresponding database in general requires significant computational resources. In addition, this database should be changed for different liquids and temperature. For this reason, one would like to have the universal database. Early it is shown that the distribution function of the intermolecular forces is well described by the hyperbolic tangent. However this function is the one-parameter. Therefore we may change the temperature of liquid, but it is not possible to vary the type of liquid (the parameters of the potential (2)). Therefore, a three-parameter (or more) distribution function is desirable. It was shown that the distribution function of the intermolecular forces can be described by the following simple function

$$P = \frac{1}{2} [\tanh(aF_i) + 1] + (bF_i^2 + cF_i^3)e^{-\alpha F_i^2}.$$  (5)

The function (5) can be used to model of different liquids. In particular the distribution function for the intermolecular forces of liquid argon described in the previous section is determined with the accuracy of about 0.5%.

The database used in the present paper was built for the system of 64000 molecules. How does the volume of the database affect the accuracy of the distribution function of the intermolecular forces? We have studied this question. The answer is simple. The volume of the database is not very
important. The discrepancy of the databases built by means of 64000 and 5000 molecules is less than 2%. Using the large number of molecules to build the database we will model better the tails of the distribution function.

The simulation accuracy of the SMM method as any method of the molecular simulation depends on the number of molecules in the simulation cell, statistics, and the computation time of one phase trajectory. The computation time of the phase trajectory must be of the order or more than the time to reach a plateau value of corresponding transport coefficient. This time is different for various transport coefficients. In general, it is impossible to predict the time to reach a plateau value of given transport coefficient. These times may vary by times.

Another important factor determining the simulation accuracy is the number of ensemble members over which the averaging is performed. The ensemble for averaging is a typical Gibbs ensemble characterized by different initial phase states of molecules with given mean values of macroscopic observables. Test calculations have shown that the simulation accuracy $\Delta_0 \sim 1/\sqrt{L}$, where $L$ is the number of ensemble members (the number of independent phase trajectories) over which the averaging is performed. As we can see, this is the expected estimate. However, it is clear that the value $\Delta_0 \sim 10^{-2}$ does not mean that accuracy of the order of one percent is achieved. The accuracy also depends on the number of molecules in the computational cell.

The dependence of the simulation accuracy of the number of particles was studied in modelling the viscosity of argon. The data obtained in simulations of 500, 1000, 2000, 4000 and 64000 molecules were analyzed. It was found that the accuracy increases with increasing the number of molecules $\Delta_0 \sim 1/\sqrt{N}$. At the same time, the calculation time increases linearly with increasing number of molecules in the cell. For a very small number of molecules, sufficiently accurate results cannot be obtained because the true plateau values of the transport coefficient (in other words the value of the transport coefficient calculated) depend on the number of molecules used.

Thus, the accuracy of SMM simulation increases with increasing both the particle number in the cell and the number of the phase trajectories used. The relative error is of an order of $\Delta \sim 1/\sqrt{NL}$. It is a pleasant fact because we can vary $N$ and $L$ independently to obtain the determined accuracy.

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