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The self-diffusion coefficient in stable and metastable states of the Lennard–Jones fluid

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ABSTRACT

Molecular-dynamics simulations have been employed to calculate the self-diffusion coefficient of a Lennard–Jones fluid for 198 sets of state parameters in the range of temperatures $0.35 \le k_BT/\varepsilon \le 2.0$ and densities $0.005 \le \rho\sigma^3 \le 1.2$. Calculations have been made in stable and metastable states to the boundary of spontaneous nucleation in a model containing 2048 interacting particles. Results of computations, performed in the parameter range of stable states, are compared with the results of previous papers. Equations have been formulated, which describe the dependences of the self-diffusion coefficient on temperature and density and on temperature and pressure in the whole range of parameters including both the stable and metastable (supersaturated vapor, superheated and supercooled liquid) states of fluid.

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1. Introduction

Models of the systems of interacting particles, employing in the description of the Lennard–Jones (LJ) potential, are traditionally widely used for the investigation of simple fluids. The LJ potential accounts for the essential features of the behavior of fluids not only in the homogeneous states (gas, liquid, crystal), but is also suitable for describing phase transitions and phase equilibria. This feature predetermines its widespread use for obtaining the information on the properties of simple substances by the methods of computer simulation for the purpose of development and improvement of liquid state theories.

At present the thermal and caloric properties of LJ systems are well established and described by equations of states. The calculation of transport coefficients of one-component LJ fluids has also been the subject of a number of computer experiments. The results of calculations of the self-diffusion coefficient D in LJ systems up to 1998 are included in the review by Liu et al. [1]. In the majority of papers (especially early ones) a study is made of the systems with relatively small sizes (from tens to several hundreds of particles) with an interparticle interaction radius not exceeding three molecular diameters as can be traced in the work of Schofield [2], Michels and Trappeniers [3,4], Chen and Rahman [5], Heyes [6,7], Hammonds and Heyes [8], Heyes and Powles [9], Borgelt et al. [10], Leegwater [11], Gardner et al. [12], Straub [13], Heyes et al. [14], Kataoka and Fujita [15], Rowley and Painter [16], Nuevo et al. [17], Canales and Padro [18]. At the same time there are calculations of transport coefficients in the systems, which contain several thousands of particles like in the paper by Erpenbeck [19,20], Heyes [21], Meier et al. [22–24].

An analysis of the dependence of the self-diffusion coefficient on the number of particles in the model system is carried out in Refs. [22–24] on the basis of the data for the systems in the range from $N = 108$ to 1372 particles. Such a dependence exists, and the disagreement between the results, obtained, for example, for the systems of 256 and 1372 particles reaches 8% on the supercritical isotherm $T^* = k_BT/\varepsilon = 3.0$ in the density range from $\rho^* = \rho\sigma^3 = 0.3$ to 0.6. Here ε and σ are parameters of the LJ potential. At densities of the gas phase the size dependence is less expressed. Thus, to bring the results of simulations closer to the properties of a macroscopic LJ fluid, one should carry out computer experiments on the calculation of transport properties in systems of the largest possible size.

There is also a weak dependence of the self-diffusion coefficient on the cutoff radius of the potential $r_c^* = r_c/\sigma$. According to the data of Refs. [22–24], such a dependence becomes negligible at $r_c^* > 4.5$.

Most comprehensive data on the self-diffusion coefficient of LJ fluids were obtained in the papers [7,15,16,22–24]. Rowley and Painter [16], Zabaloy et al. [25], Suarez-Iglesias et al. [26], based on the results of simulations, derived equations, which describe the dependence of the product $D^*\rho^*$ self-diffusion times density on temperature and density.

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One of the tasks of the present investigation is to calculate the self-diffusion coefficient in the metastable states of LJ systems (supersaturated vapor, superheated and supercooled liquid) up to the boundaries of the limiting supersaturation, beyond which one can observe condensation, boiling-up and crystallization of a homogeneous fluid. All calculations have been performed with a cutoff radius of the potential of no less than 5.975σ. Allowance for weak interactions at large interparticle distances is of fundamental importance in the simulation of metastable and near-critical states. Another task of the paper is to obtain an analytical dependence of the self-diffusion coefficient on temperature, pressure and density comprising both stable and metastable states of LJ fluid.

2. Simulation procedure

The simulation was carried out by the method of equilibrium molecular dynamics (MD) in *NVE* ensemble, where *N* is the number of particles, *V* is the volume, *E* is the energy of the system. All calculations are executed with $N = 2048$ in a cubic cell with periodic boundary conditions. The particles interact through the truncated Lennard–Jones potential

$$u = \begin{cases} 4\varepsilon\left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^{6}\right], & r \le r_c \\ 0, & r > r_c \end{cases}. \tag{1}$$

The cutoff radius of the potential is $r_c = 6.78\sigma$ at $\rho^* < 0.82$ and equals half of the cell edge at large densities, but no less than 5.975σ ($\rho^* = 1.2$).

Further all quantities are presented in reduced units. Such reduced parameters are specified by the sign (*): temperature $T^* = k_BT/\varepsilon$, density $\rho^* = \rho\sigma^3$, pressure $p^* = p\sigma^3/\varepsilon$, self-diffusion coefficient $D^* = D\sqrt{m/\varepsilon\sigma^2}$, where k_B is the Boltzmann constant, *m* is the mass of a particle.

To integrate the equations of particle motion use was made of the Beeman algorithm [27]. The integration time step was $\Delta t^* = \sqrt{\varepsilon/m\sigma^2}\Delta t = 0.0046$ at temperatures $T^* > 0.35$. At $T^* = 0.35$ we have $\Delta t^* = 0.0023$.

The pressure was calculated with allowance for the correction for long-range interactions, $\Delta p^* = -16\pi\rho^{*2}/3r_c^{*3}$, obtained in the approximation of the absence of correlation in interaction of particles at the distances $r^* > r_c^*$.

The self-diffusion coefficient was calculated from the Einstein relation through the mean-squared particle displacement [28]

$$D_r = \lim_{t\to\infty}\frac{1}{6N}\frac{d}{dt}\left\langle \sum_{i=1}^{N}\left[\vec{r}_i(t) - \vec{r}_i(t_0)\right]^2 \right\rangle \tag{2}$$

and by the Green–Kubo formula through the integral with respect to time of the velocity autocorrelation function [28]

$$D_v = \frac{1}{3N}\int_0^\infty \sum_{i=1}^{N}\left\langle \vec{v}_i(t)\vec{v}_i(t_0)\right\rangle dt, \tag{3}$$

where $\vec{r}_i$ and $\vec{v}_i$ are the radius-vector and the particle velocity. The angular brackets indicate averaging over the finite sections of the trajectory of the system in phase space with the initial moments of time, t_0. Mean-square particle displacements were calculated with the use of an additional data array, which made it possible to retain in a system with periodic boundaries the continuity of the trajectories of motion of particles when they went beyond the boundaries of the basic cell. The total momentum vector of the system $\vec{P}^*$ was set to zero before every simulation so that the system as a whole was at rest. The algorithm [27] ensures the fulfillment of the condition $|\vec{P}^*| < 10^{-10}$ on intervals $\sim 10^6\Delta t^*$. In such a way the contribution of the motion of the system as a whole to the particle displacements was excluded.

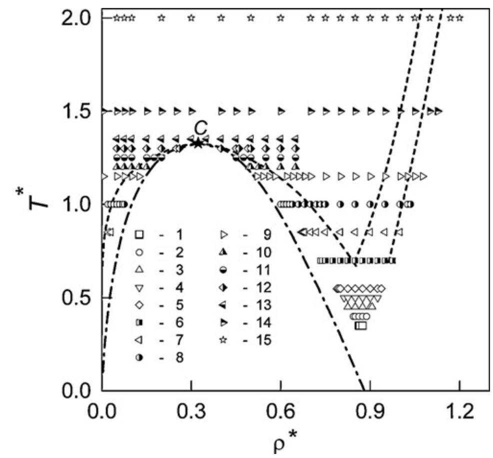

Fig. 1. (T^*,ρ^*)-projection of the phase diagram of a LJ system. The symbols show the states investigated along the different isotherms: (1) $T^* = 0.35$, (2) 0.4, (3) 0.45, (4) 0.5, (5) 0.55, (6) 0.7, (7) 0.85, (8) 1.0, (9) 1.15, (10) 1.2, (11) 1.25, (12) 1.3, (13) 1.35, (14) 1.5, (15) 2.0. Dashed lines refer to liquid–gas and liquid–crystal phase equilibrium lines. Dash-dotted lines represent the spinodals of supersaturated vapor and superheated liquid. *C* is the critical point.

Calculations have been carried out along 15 isotherms for 198 states of the system in the temperature range between $T^* = 0.35$ and 2.0. The initial states on each isotherm were selected at densities corresponding to a stable liquid or gas except the isotherms $T^* < 0.55$, on which all states are metastable. A transition to the neighboring states on an isotherm was realized by consecutive compression (stretching) of the cell and scaling of the particle coordinates. In the calculation, for every new point the final configuration of the previous point on the isotherm was taken as the initial configuration of particles. The change in density was decreased with increasing degree of metastability. The time of equilibration depended on the thermodynamic state of the system (i.e., whether the state was stable, metastable, near-critical) and varied in the range from 250 to 350 thousand steps of integration of the equations of motion. Calculations were performed up to the densities at which metastable states collapsed for the characteristic time of a computer experiment.

The parameters of calculation of the velocity autocorrelation function and mean-square particle displacement depended on the state parameters of the system under investigation. The values of the respective functions were calculated every second time step of integration of the equations of motion at densities $\rho^* > 0.3$, every 10th time step in the range of densities $0.2 < \rho^* \le 0.3$, every 20th time step in the range of densities $0.1 < \rho^* \le 0.2$, and every 50th time step in the range of densities $0.005 \le \rho^* \le 0.1$. Every function was determined for one thousand values *t* and averaged over 250 initial times, t_0. The described procedure of calculation made it possible in all states to reach a full relaxation of the velocity autocorrelation function and to over to the linear regime of the dependence of mean-square particle displacement on time.

3. Results and discussion of calculations of the self-diffusion coefficient

The investigated states are presented on the (T^*,ρ^*)-projection of the phase diagram (Fig. 1). Stable and metastable states of the LJ fluid are separated by the liquid–gas and liquid–crystal phase equilibrium curves. The liquid–gas phase equilibrium curves have been constructed based on the results of simulation of a two-phase LJ liquid–gas system by Baidakov et al. [29]. The liquid–crystal coexistence line has been established employing the results of Baidakov and Protsenko outlined in [30]. The boundaries of essential instabil-

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