Simulation of liquid Rb by the methods of classical and first-principle molecular dynamics and statistical geometrical analysis of the atomic structure models using the Voronoi-Delaunay method

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Simulation of liquid Rb by the methods of classical and first-principle molecular dynamics and statistical geometrical analysis of the atomic structure models using the Voronoi-Delaunay method

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Abstract. The atomic structures of liquid rubidium were simulated by classical and first-principle Molecular Dynamics methods for a range of temperatures. The pair potentials necessary for the Classical Molecular Dynamics calculations were obtained using diffraction data by the Schommers iterative method. In all cases simulated pair correlation functions and structure factors correctly reproduced the experimental ones. A Delaunay simplex, comprised by four atoms, is the simplest element of the structure. All atomic aggregates in an atomic structure consist of them. The structure factor of the simplicial voids system is additional structural characteristic which allows seeing distinction in structures with almost similar pair correlation functions.

1. Introduction

There is a series of methods for obtaining models of atomic structure. The most straightforward and well-founded methods are the group of Ab-initio Molecular Dynamics methods (ab-initio MD). Electronic and atomic structures are found simultaneously in these methods. But at the same time the Ab-initio MD methods are the most computational burden. They allow performing simulation with models up to 100–500 atoms only.

Another group of methods consists of Classical Molecular Dynamics (MD) and Monte-Carlo (MC) methods. They could work with a huge amount of particles (up to 10^8), but require the form of inter-atomic interaction. The main problems of the methods are unknown shape of the potential function and strong dependence of potential function

on density and temperature. Usually the simplest spherically symmetric pair interaction is chosen, but there are some attempts to take density changes into account (Embedded Atom Method [1] or indirect dependence of potential parameters on density [2]).

Methods of Reverse Monte-Carlo (RMC) [3] and Schommers Molecular Dynamics (Schommers MD) [4] are related to the third group of methods for obtaining atomic structure. These methods fit atomic positions to experimental structural data (structure factor or radial distribution function) directly, so they make an atomic model corresponded to the experimental results. These methods are quite fast, so models with several thousands of atoms could be constructed easily. Moreover Schommers method restores the effective pair potential for established conditions, so it could be used for further investigation of the dynamics of the model.

Recently the precise structural data for liquid Rubidium have been obtained [5] experimentally. The temperature and density range of experimental data covered the whole range of liquid rubidium existence from the melting point up to the critical point. So the interesting possibility for comparison of ab-initio MD and Schommers MD has appeared.

2. Methods

The SIESTA package [6] was used for ab-initio MD. The algorithm realization and usage of the atomic orbitals basis set resulted to the linear dependence of calculation time on the size of the system. Periodical boundary conditions on a cubic supercell have been used. We took 300 atoms per a supercell for high temperatures and 200 atoms per a supercell for low temperatures. The molecular dynamics time step was 5 fs. The time for system relaxation was 1.0 ps. The time for statistics accumulation was 1.0 ps.

For Schommers method we used LAMMPS [7] molecular dynamic simulation package together with hand-made procedure for potential correction. Potential correction is based on convergent Schommers algorithm [4]:

$$\phi^{(0)}(r) = -kT * lg[g(r)],\ \phi^{(n+1)}(r) = \phi^{(n)}(r) + kT * lg\left(\frac{g^{(n)}(r)}{g(r)}\right), \qquad (1)$$

where $g(r)$ is the experimental (target) radial distribution function, $\phi^{(n)}(r)$ is the pair potential on n-th iteration, $g^{(n)}(r)$ is the radial distribution function for a model with the potential $\phi^{(n)}(r)$.

We used a model with 4000 atoms. The time step was 7 fs. The time for system relaxation was $\approx$ 10 ps. The time for statistics accumulation was $\approx$ 20 ps. The number of iterations was $\approx$ 100.

The comparison and analysis of the models were made by traditional (radial distribution function, structure factor) methods and by statistical geometrical Voronoi-Delaunay method [8]. This method is based on the tessellation of the whole space into regions of simple geometric shapes (Voronoi polyhedra or Delaunay simplexes), containing information about the mutual arrangement of atoms, and further statistical investigation of these regions.

3. Results and discussion

In Fig. 1 the radial distribution functions of the models are compared with the experimental ones. It could be seen that both model radial distribution functions are in a good agreement with the experiment for all temperatures. Statistics of Voronoi polyhedra were obtained for both series of models. Both methods gave almost the same results. No peculiarities on statistical curves were observed.

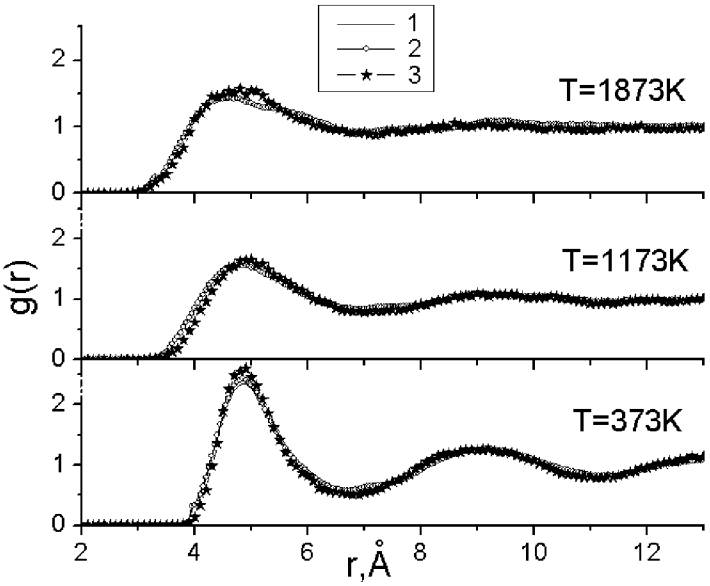

Figure 1. Radial distribution functions: 1 – experiment, 2 – Schommers method, 3 – Ab-initio MD

The Delaunay simplex is found to be more informative for the structure description than the Voronoi polihedra. In the work [9] it was suggested to investigate the relative arrangement of simplices or simplicial voids. It appears that the void-void structural factor is an additional useful structural characteristic. It allows to find out the difference between structures with similar atom-atom radial distribution functions.

In figure 2 the void–void structural factor is shown. It could be seen that structural factor changes shape at the high temperatures. The main peak splits into two peaks. It was found [10] for liquid Cs, that the peak 2 appears due to the forming of the pseudomolecular pairs of atoms. The peak 1 fits with homogeneous structure and the peak 2 fits with inhomogeneous (pseudomolecular) structure.

4. Conclusions

We performed the simulation of the atomic structure by ab-initio MD and Schommers MD. Both structures are in good agreement with the results of the diffraction experiment. Void-void structure factor obtained from Delaunay tesselation shows transition in liquid Rb from a uniform liquid at low temperatures to a liquid with inhomogeneous structure at high temperatures.

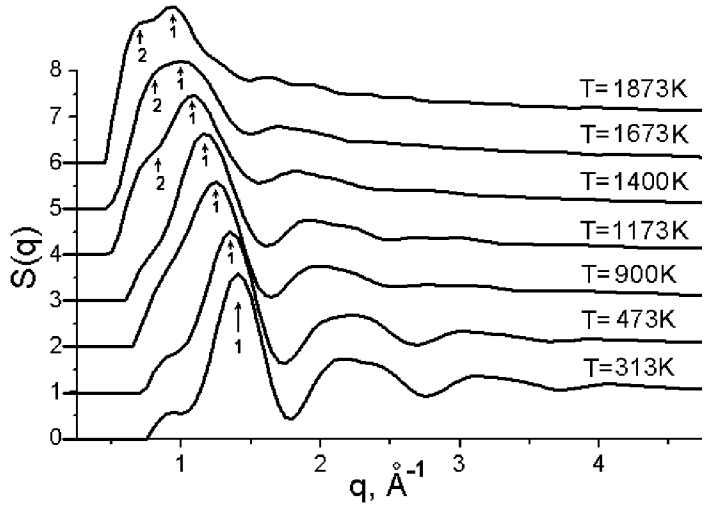

Figure 2. Void-Void structural factors for Ab-initio models.

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