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IN MEMORY OF G.A. MARTYNOV

Molecular Dynamics Simulation of Argon and Argon–Water Systems

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Abstract—A molecular dynamics model is created for argon near the critical point. As the temperature falls at a constant density less than critical, It is established that a drop of liquid argon forms in the gas environment. This drop is not spherical, but cylindrical. Liquid argon near the melting point (110 K, density 1.513 g/cm^3) is also modeled. The values of the Voronoi polyhedra volumes (VPVs) around argon atoms are calculated and their distribution is plotted. The VPV values lie in the range of 34–55 Å^3, with an average value of 43.6 Å^3. Argon atoms with low VPV values tend to combine with one another and form branching clusters, as is typical of atoms with high VPV values. Clusters formed by atoms with high and low VPV values are inserted into one another. Issues related to the behavior of argon atoms in argon–water systems are also considered.

Keywords: molecular dynamics, argon, water, Voronoi polyhedral

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INTRODUCTION

At the request of G.A. Martynov, a molecular dynamics simulation of argon near the critical point was performed, and the stratification of a homogeneous system into vapor and liquid was followed as the temperature fell below critical several times and at several densities. This work discusses the results for a temperature of 110 K (−163°C) and a density of 0.3 g/cm^3. Calculations for are also performed for liquid argon, clathrate hydrate, and a water film in an argon atmosphere. Most of the results have been published, but this work considers some aspects that were not covered sufficiently in them.

CALCULATION PROCEDURES

Systems consisting only of argon atoms were modeled using the program provided by N.K. Balabaev. Modeling was done in the *NTP* ensemble. To select the parameters of the Lennard-Jones potential describing the interactions, trial calculations were performed for crystalline and liquid argon at $T = 100$ K. Parameters were chosen such that the densities of these phases were close to experimental values. The density of crystalline argon at 92 MPa was 1.699 g/cm^3, while the density of liquid argon at 73 MPa was 1.489 g/cm^3. These values were very close to the experimental data [1]. Numerical values of the parameters of potential functions were given in [2, 3]. Systems containing argon atoms and water molecules were modeled in the microcanonical ensemble using the program compiled by E.A. Zheligovskaya and modified by the author. Interactions between water molecules were described using the potential function proposed in [4]. The parameters of the argon–oxygen and argon–hydrogen potential functions were selected by the author [2, 3]. A program developed and provided to the author by

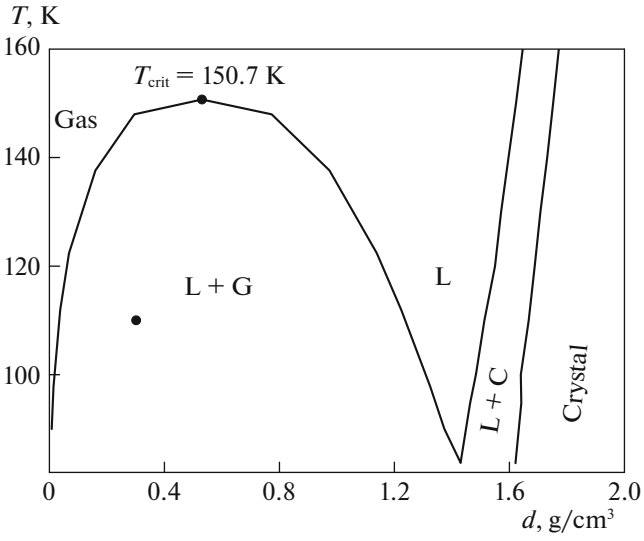

Fig. 1. Phase diagram of argon.

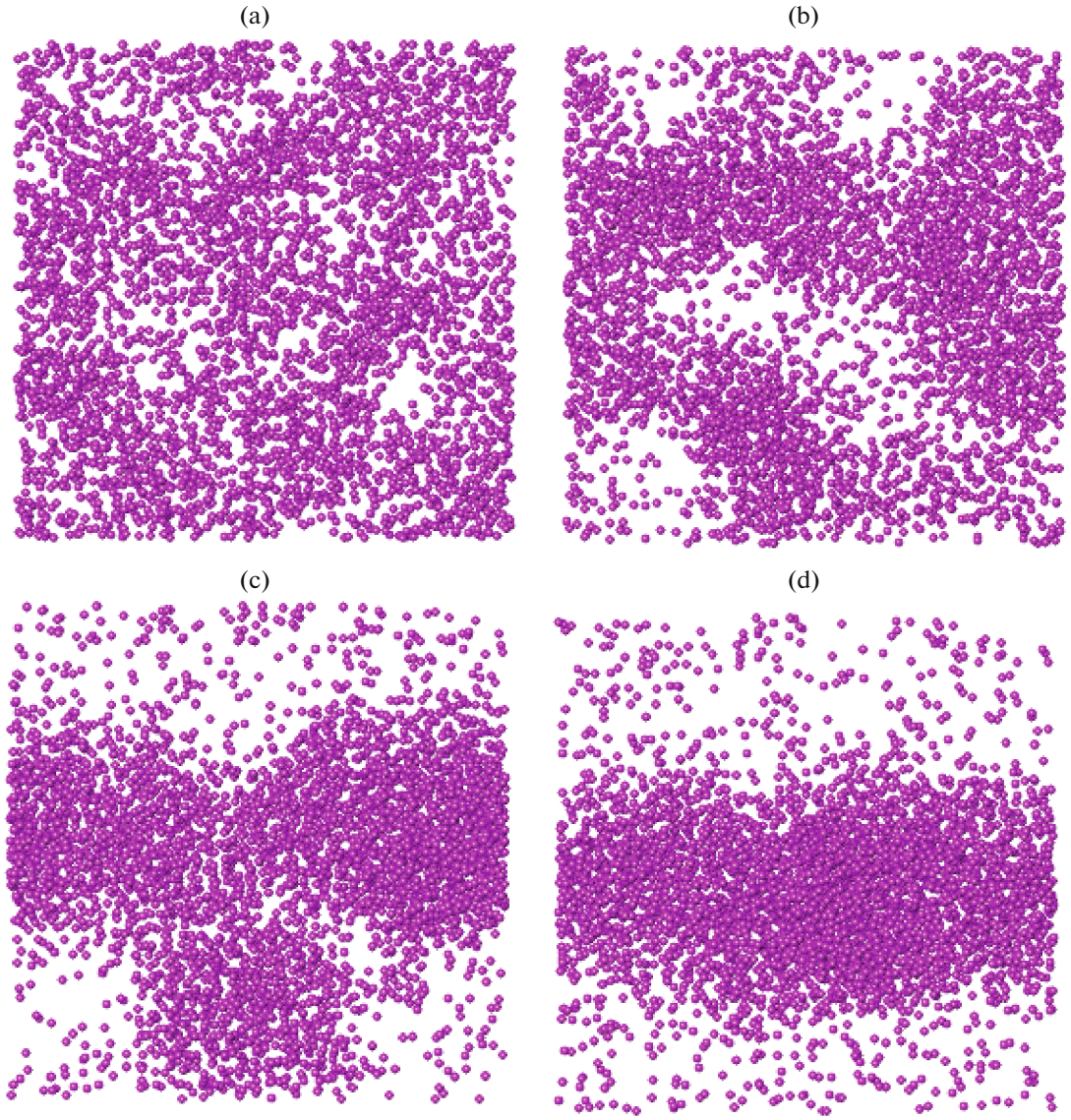

Fig. 2. Stratification of argon at 110 K (density, 0.3 g/cm^3) into liquid and vapor over time. Step of integration, 1 fs; intervals between frames, tens of ps.

V.P. Voloshin were used to calculate the volumes of Voronoi polyhedra.

Modeling Argon at a Temperature Slightly Below Critical

Figure 1 shows a phase diagram of argon in temperature–density coordinates. The data discussed below were obtained for a temperature of 110 K (−163°C) and a density of 0.3 g/cm^3 (the point on the phase diagram).

The modeling of argon (4000 atoms in a periodic cubic cell) began at a temperature slightly above the critical temperature (150.3 K), based on a homogeneous fluid (the atoms were uniformly distributed in space). The temperature dropped sharply to 110 K, and the system began to separate gradually into vapor and liquid (Figs. 2a–2c). A cylindrical drop surrounded by vapor formed as a result (Fig. 2d).

A tendency of this drop to transform into a spherical one began to emerge after a long period of modeling (Fig. 3), but we did not wait for the formation of a spherical drop.

Modeling Liquid Argon

The results from modeling argon near the melting point are discussed below (temperature, 110 K; density, 1.513 g/cm^3). Argon under these conditions is not

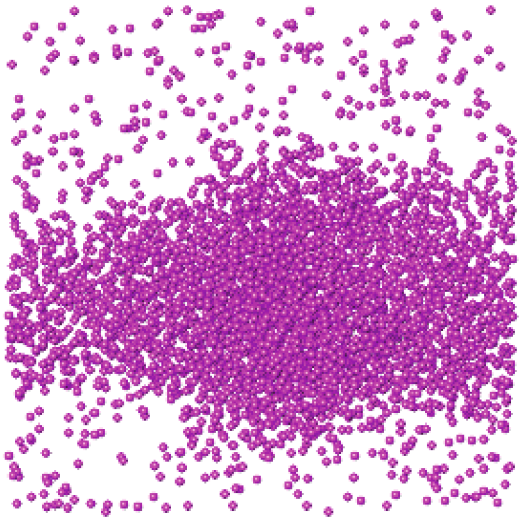

Fig. 3. Start of the formation of a spherical drop.

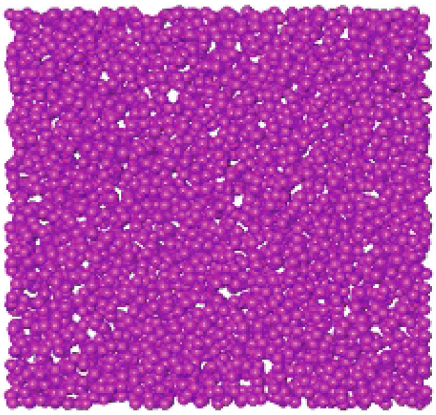

Fig. 4. Snapshot of liquid argon (T = 110 K; density, 1.513 g/cm^3) with 4000 atoms in a periodic cubic cell.

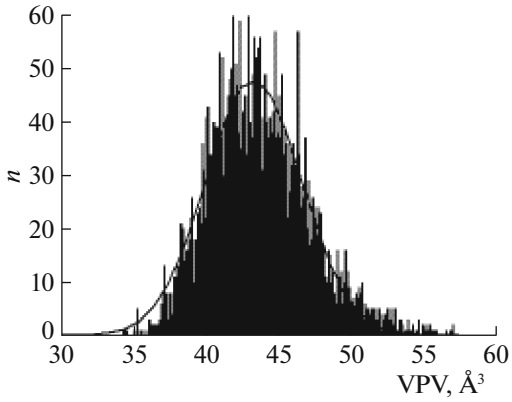

Fig. 5. Voronoi polyhedra volume (VPV) distribution in an instantaneous liquid argon configuration of 4000 atoms. Gaussian curve fitting is shown.

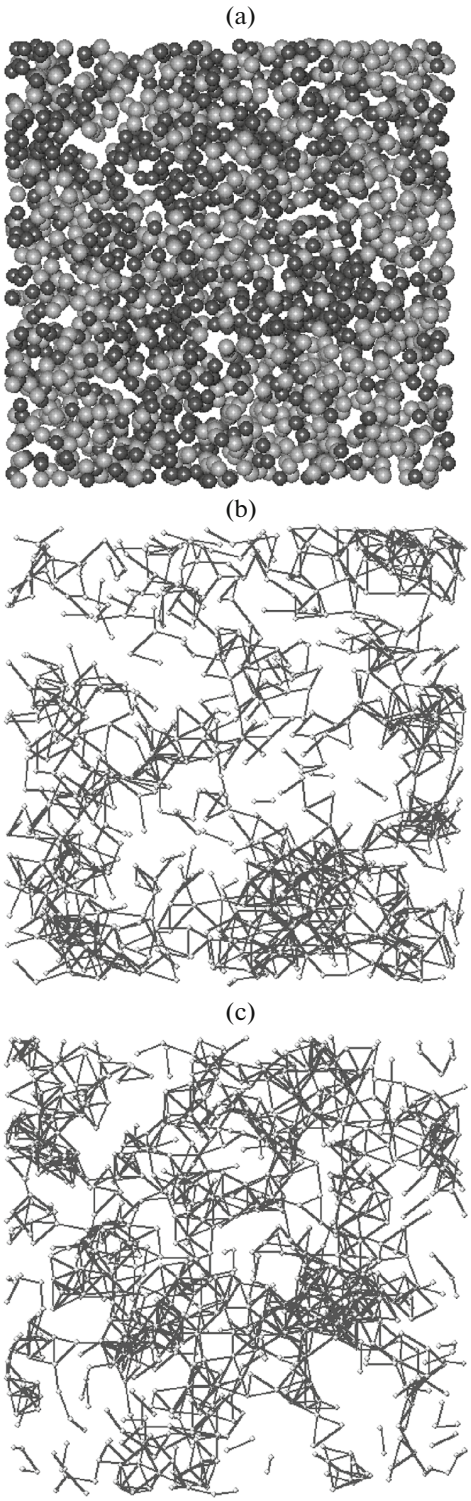

Fig. 6. (a) Argon at 110 K, d = 1.513 Å, and 4000 atoms. Coloring of atoms according to Voronoi polyhedron volume (VPV): black spheres, VPM < 41.37 Å^3; grey spheres, VPV > 45.97 Å^3; 1000 atoms of each type. (b) The same configuration of atoms with VPV > 45.97 Å^3 and neighbors separated by no more than 4 Å (a total of 906 atoms connected by bonds). (c) The same configuration of atoms with VPV < 41.37 Å^3 and neighbors separated by no more than 4 Å (a total of 942 atoms connected by bonds).

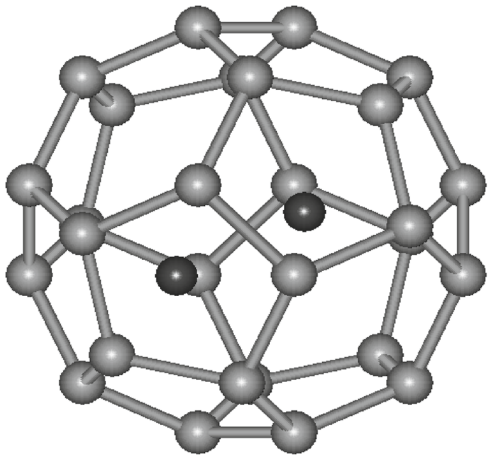

Fig. 7. Two argon atoms in a large cavity of clathrate hydrate.

uniform in density, as can be seen in the snapshot (Fig. 4). To study this inhomogeneity, we calculated the volumes of Voronoi polyhedra (VPVs) [5]. The more VPVs a given atom has, the lower the local density in the place where this atom is located. The VPV values of liquid argon lay in the range of 34–58 Å^3 (Fig. 5).

Figure 6 shows an instantaneous configuration in which the argon atoms are colored grey and black, depending on the VPV values. Figure 6a shows the 25% (1000 atoms) with the lowest VPV values (black) and 25% (1000 atoms) with the highest VPV values (grey). We can see the black atoms are grouped together, and the grey ones are grouped together as well. For convenience of consideration, atoms of each type in Figs. 6b, 6c are connected by nominal bonds no longer than 4 Å. We can see that the atoms of each type form three-dimensional grids inserted into one another.

At comparatively low pressures, argon forms a clathrate hydrate with CS II structure [6, 7]. Large 14-facet cavities contain two argon atoms each (Fig. 7) [6, 7].

Other argon hydrates are considered in [3]. According to our modeling results, these atoms move inside a cavity while the distance between them oscillates around an average value of 3.45 Å with a period of ~0.3 ps (Fig. 8a). There are two areas in the cavity where argon atoms prefer to be located. Sometimes the atoms change places (Figs. 8b, 8c). This movement of atoms from one region to another does not affect the temporal dependence of the distance between atoms. Small (dodecahedral) cavities contain one argon atom each. The movement of argon atoms from one cavity to another was not observed.

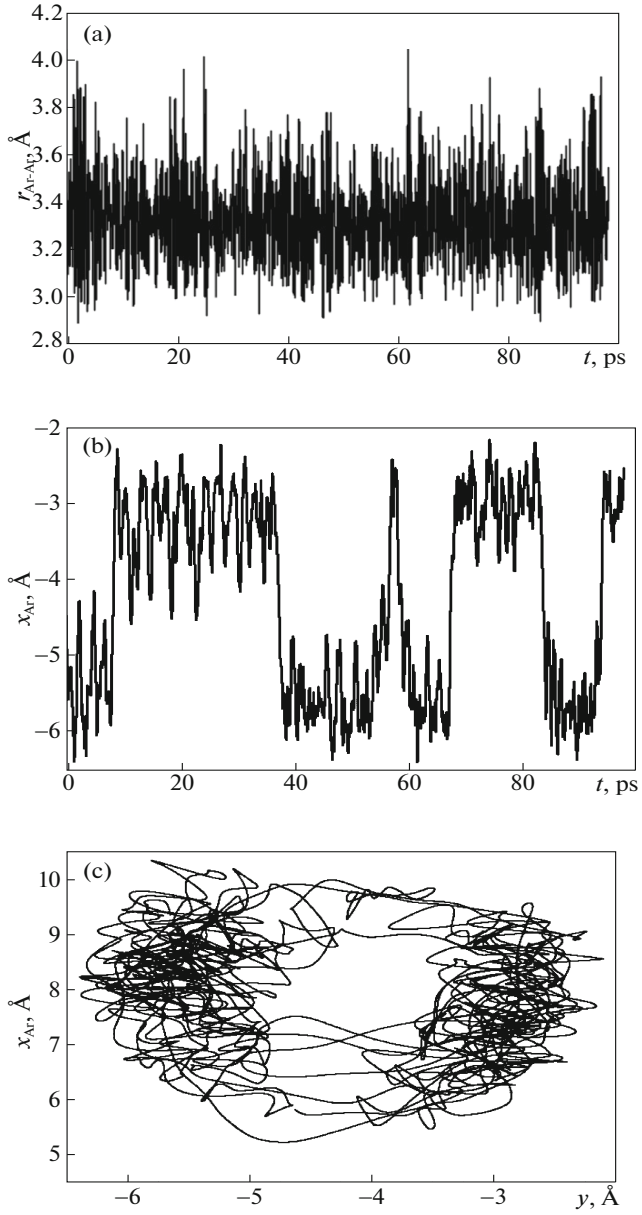

Fig. 8. (a) Temporal dependence of the distance between argon atoms inside a large cavity of the CS II clathrate framework (T = 267 K, average distance is 3.45 Å). (b) Temporal dependence of coordinate x of an argon atom in a large cavity of the CS II framework. (c) Dependence of coordinate x of an argon atom in a large cavity of the CS II framework on coordinate y of the same atom.

Contact pairs of argon atoms formed in both liquid aqueous solutions of argon and aqueous films [8] in an argon atmosphere (Fig. 9). Amorphous ice or amorphous films that contained single argon atoms, contact pairs, and sometimes larger groups of argon atoms formed at low temperatures [3, 8]. The motion of argon atoms in contact pairs captured by amorphous ice was of the same character as in clathrate hydrate.

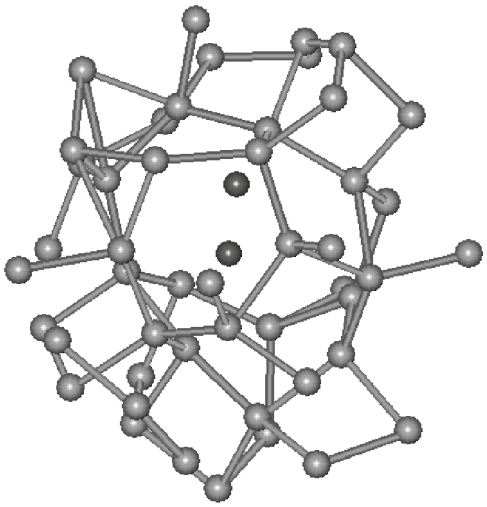

Fig. 9. Contact pair of argon atoms surrounded by water molecules (grey spheres are oxygen atoms) in an aqueous solution of argon.

CONFLICT OF INTEREST

The author declares he has no conflict of interest.

OPEN ACCESS

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