



Structure and Dynamic Inhomogeneity of Liquids on the Liquid–Gas Coexistence Curve Near the Triple Point

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Abstract The paper proposes a method based on a combination of the provisions of the phonon theory of liquid, V–T formalism, and Frenkel’s theory of determining the P–T parameters of a liquid system, to determine the pressure and temperature values at which the transition from a denser liquid fraction to a less dense one occurs. Its use makes it possible to analyze the motion of fluid components in joint complexes and to determine their lifetime. It is also shown that at short time intervals, regardless of the physical state of the system, the components of the liquid move as independent particles, and their motion can be represented within the framework of the vibrational-hopping diffusion model. In this paper, the developed methodology is used to study the structural and dynamic properties of argon near the triple point on the liquid–gas coexistence curve.

Keywords argon · coexistence curve · diffusion · molecular dynamics

1 Introduction

Theoretical description of liquids structures and their motion has been puzzling the researchers in the field of the liquid state physics for many years.^[1–6] One of the particular problems within this objective is the study of the structural and dynamic processes near critical points, in which several phases of the matter coexist.^[7–9] According to van der Waals, the idea of critical points in liquids “is based upon a hypothesis rather than a thermodynamic definition. Moreover, no one has ever succeeded in measuring a critical density of an atomic or molecular fluid directly. Liquid–gas critical densities are only obtained experimentally indirectly by an extrapolation of a mean of the two coexisting densities of liquid and gas using the law of rectilinear diameters “. ^[10] Taking into account the absence of the conceptual problems with the definition of the triple-point, the intersection of the liquid–gas and the solid–gas coexistence lines on the *P–T* diagram, we have chosen its vicinity in order to study the structural–dynamic properties of a liquid on liquid–gas coexistence curve when changing P–T state of the system. In the triple point state, three phases (gas, liquid and solid) of a pure substance exist in thermodynamic equilibrium. The vicinity of the triple point on the coexistence curve has been widely used to understand the ordering and metastability during melting and freezing phenomena.^[11,12]

The study of the structure and motion of such disordered systems is one of the most important problems in fluid physics, in which the motion of molecules is both collective and individual. During phase transitions in liquid systems with an increase in temperature, the structure changes with a decrease in the proportion of close packing, which leads to a transition from «dense liquid» fractions to «less dense» ones. In this case, the disordered motions of

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particle clusters at temperatures above the melting point (either due to changes in temperature, pressure or due to changes in density) demonstrate heterogeneous dynamics. However, there is still no method for determining the physical conditions under which both structural and dynamic transformations occur during the transition from denser to less dense liquid fractions in the course of processes both in the region of critical points and on the coexistence curve.

In this research, we begin with an assumption that the microstructure of the liquid near the triple point on the liquid–gas coexistence curve contains components of a dense liquid, as well as a liquid and a gas. The increase in the temperature and pressure on the coexistence curve in this region leads to changes in the structural properties of the system, in particular, in the transition from the structure that is characteristic of the “dense liquid” to the “liquid” structure with the “gas-like” liquid components. An excellent model system for studying the phenomena described above are simple liquids, which form a wide class of disordered systems; primarily they include inert gases and several molecular gases. In them, the interparticle interaction potential can be considered paired, spherically symmetric, and non-saturable. Many of them are used in technological processes across a plethora of industries.

When studying such complex systems, ‘scaled particle’ models of monatomic liquids are used. Knowing what changes in the properties of such liquids are induced by the change in the thermodynamic parameters of the system, can greatly assist the use and improvement of the above mentioned processes.

These models successfully describe the behavior of both model and real liquids. One of such monoatomic model liquids is argon, a classic simple system to test theoretical predictions and to study the fundamental properties of liquids, dating back to the classical works of Rahman^[13] and other researchers.^[14,15] Argon is spherical, it has no dipole moment, demonstrates an inert behavior, has a small quantum effect, and is thus a great reference substance for the model representation in describing and predicting the thermodynamic properties of the systems of great technical importance.^[16–18] Thus, the properties of argon on the coexistence curve near the triple point attract a wide attention.^[14,19–22] Among them are the works of Levesque et al.^[23,24] on the autocorrelation function of the shear viscosity at the triple point of argon and that of Heyes,^[25] in which molecular dynamics was used to compute the transport coefficients of argon for different parts of its phase diagram. Bandyopadhyay et al.,^[26] in turn, offered a systematic analysis of the experimentally obtained data for the thermodynamical behavior of argon near the triple point. The authors of Ref 27, 28 demonstrated that an

increase in temperature and the pressure of the system leads to the simultaneous presence of «dense liquid», liquid and «gas-like liquids» elements in thermodynamic equilibrium on the coexistence curve. Based on Ref 11–26, we can expect that the change in temperature on the liquid–gas coexistence curve on the P–T diagram leads to the change in liquid dynamics, in particular, its change from the «dense liquid» → «liquid-like» → «-gas-like» dynamics.

As the state of a system near its critical point can be determined by calculating a combination of equilibrium structural characteristics as well as the kinetic thermo-physical parameters (mean-square displacement, diffusion coefficient, velocity autocorrelation function, etc.), presently we describe the calculated values of physical properties of the argon on the coexistence curve, for which the structure of the system and its time dynamic heterogeneity change. In what follows, using argon as an example, we present a method: determining the P–T parameters on the liquid–gas coexistence curve at which the mechanism of particle motion in the liquid changes at which the mixture transitions from the “dense liquid-like” to “liquid-like” and then “liquid–gas-like” regime; determining the duration of the movement of fluid components in the composition of joint complexes and constructing model representations to describe diffusion at various time intervals for P-T parameters states on the liquid–gas coexistence curve.

2 Molecular Dynamics Simulation

As argon is uniform it gives rise to no force on any molecule, so that at fixed density the system behaves exactly like a Lennard-Jones fluid,^[29,30] so the intermolecular interaction in such systems^[31] can be modeled by Lennard-Jones potential:

$$U = U_{LJ} = \sum_{ij} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (\text{Eq 1})$$

where $\sigma_{ij}, \epsilon_{ij}$ are Lennard-Jones interaction potentials and r_{ij} is the inter-particle distance. Molecular dynamics (MD) simulation of argon systems was carried out using the DLPOLY_4.05 software package, i.e. we fixed the number of argon particles, the temperature, and the volume of the system. The numerical integration of the equation of motion was implemented by the Varlet algorithm with a time step of 2 fs. The periodic cubic cell contained 256 argons. The simulation was performed mainly in an NVT ensemble at different densities and temperatures. The temperature was maintained constant using a Berendsen thermostat^[32,33] with a “P,T coupling” algorithm, which incorporates the SHAKE algorithm.

The following accelerated equilibration three-step strategy was applied: In step 1 an initial configuration of 256 argons was manually constructed at selected lattice positions within a cubic simulation box of side 23.9 Å. The density of the argon system was chosen to correspond to the experimental value of argon density at $T = 110$ K. Its parameters were determined by trial calculations of crystalline and liquid argon at 100 K. The density of crystalline argon at a pressure of 92 MPa was 1.699 g/cm³, and the density of liquid argon at this temperature and a pressure of 73 MPa was equal to 1.489 g/cm³. These values are close to the experimental data listed in Ref 34. The initial configuration was then equilibrated at $T = 110$ K with a constant NPT simulation for 1×10^6 runs. The final configuration at $T = 110$ K was then re-equilibrated under constant NVT conditions for 1.5×10^6 runs. Next, in step 2 the final configuration at $T = 110$ K from step 1 was used as the initial configuration into the system at $T = 105$ K at a cubic simulation box (of side 23.7 Å). This configuration was equilibrated at $T = 105$ K with a constant NPT simulation for 1×10^6 runs. The final configuration at $T = 105$ K was again re-equilibrated under constant NVT conditions for 1.5×10^6 runs. Lastly, in step 3 the final configuration at $T = 105$ K obtained during step 2 was used as a pre-equilibrated configuration and run under constant NVT conditions for 1.0×10^6 runs as a production run with a time step 2.0 fs. When carrying out the analysis of the structural and dynamic properties of the system, a total of 2115 configurations were analyzed. A similar algorithm was used to carry out calculations at $T = 100$ K, $T = 95$ K, $T = 90$ K, $T = 85$ K on the coexistence curve near the critical point. For each of these temperatures, the calculation box size was recalculated to match the density of argon at this temperature and pressure. Energy, temperature, and pressure were monitored during the time of the calculation and shown to be well established, with only small fluctuations typical for MD simulations.

3 Results and Discussion

The study of the structural-dynamic properties of liquid systems acts as a bridge connecting the study of microscopic and macroscopic properties of liquids. With this in mind, in this article we studied the correlation between changes in the structure and dynamic inhomogeneity of argon on the liquid–gas coexistence curve near the triple point ($T = 83.8$ K).^[35]

The physical conditions, namely, the pressure and temperature values on the liquid–gas coexistence curve under which the structure of argon changes near the triple point on the liquid–gas coexistence curve, namely, the transformation of the “dense liquid” to “liquid-like », are

still unknown. Taking this into account, at the first stage of research, an analysis of the structural properties of argon was carried out on the liquid–gas coexistence curve. The transition from one liquid structure to another is determined by a change in the local order and dynamic behavior across systems.

In order to obtain the information described above, the radial distribution functions (RDFs) were calculated for argon and its structural peculiarities were determined at $T = 85$ to 110 K on the coexistence curve. During the second stage, the analysis of the kinetic properties of argon in the chosen range of temperatures and pressures was carried out and the model representations to describe the temporal and thermal heterogeneities of diffusion on the coexistence curve were developed.

3.1 Local Structure of Argon Near the Triple Point on the Coexistence Curve

The increase in the temperature along the coexistence curve leads to the change in the local structure of the liquid, whose analysis was carried out using the RDF $G_{XY}(r)$. The RDFs gives a probability of finding particles of type y near particles of type x , and can be calculated using the following equation^[31]:

$$G_{XY}(r) = \frac{\langle N_y(r, r + dr) \rangle}{4\pi\rho_y r^2 dr} \quad (\text{Eq 2})$$

In this equation, the numerator describes the average number of particles y in a spherical layer ($r, r + dr$), and the denominator normalizes the distribution, so that $G_{XY}(r) = 1$ at $N_y = \rho_y$, where ρ_y is the density of the system.

The RDF of argon on the coexistence curve (Fig. 1) shows that the temperature change has practically no effect on the position of the RDF first maximum, which correlates with the notion of the negligibly small changes in the structure of the monoatomic liquids during the change of temperature along the coexistence curve near the melting point. The authors of Ref 27 confirm this both experimentally and using calculation with a quasi-crystalline (QCM) approach while studying the short-range order structure of argon near its melting point at 85.0 K.

All RDFs (shown in Fig. 1) can be classified into two groups: the first one for $T < 90$ K, and the second one for $T > 90$ K. Within each group the values of $G_{XY}(r)$ decrease inside the boundaries of the second and the third coordination spheres. At the same time, the minima of the RDFs increase, pointing at the lowering of the order in the system. The analysis of RDF shows that the increase in the temperature of the system on the liquid–gas coexistence curve near the triple point leads to the following: a small decrease in the size of the first coordination sphere (the first

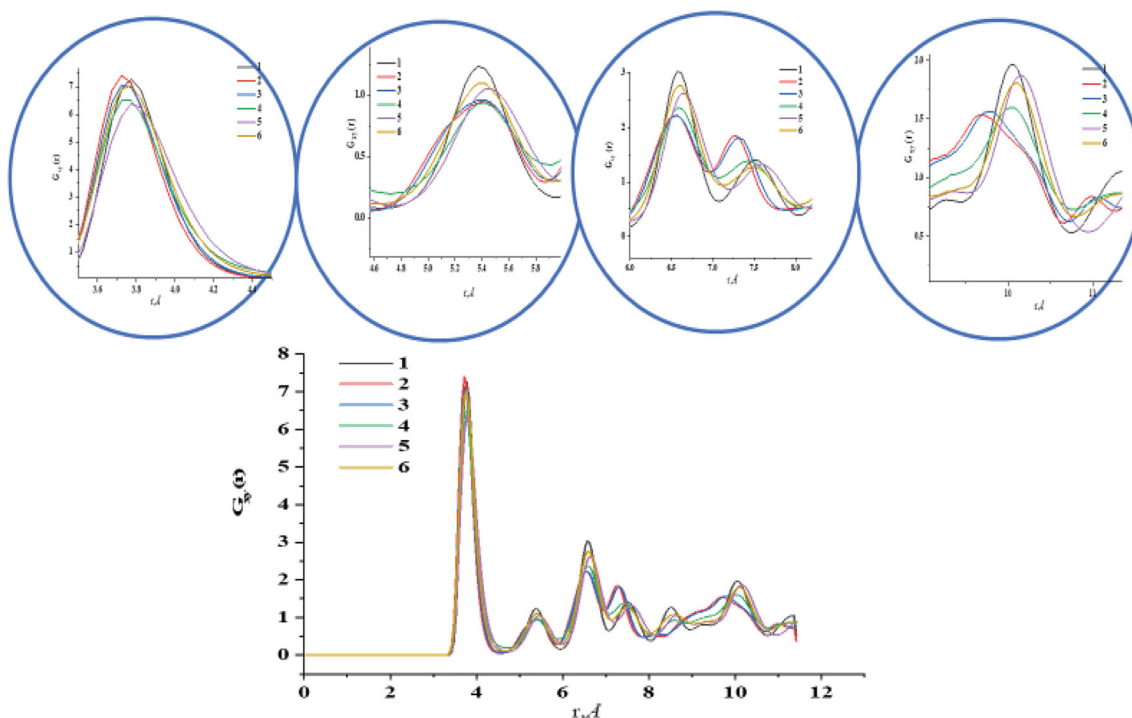


Fig. 1 Radial distribution function $G_{XY}(r)$ between the center of mass of argon at temperatures 85 K (1), 90 K (2), 95 K (3), 100 K (4), 105 K (5), and 110 K (6). Blue circle inserts show the first, second, third, fourth, and fifth maxima of $G_{XY}(r)$ (Color figure online)

minimum of RDF is at $r_{min} = 4.9 \text{ \AA}$) and a similar decrease in the size of the second coordination sphere (the second minimum of the RDF is at $r_{min} = 5.9 \text{ \AA}$); the change in the shape of the RDF and the change in the position of the fourth maximum and the fourth minimum of the RDF, supporting the notion about the change of the argon structure at relatively large distances.

The change in the physical characteristics of the system (such as temperature and pressure) on the coexistence curve near the triple point leaves the distance between the closest argon atoms unaffected at $\sim 3.8 \text{ \AA}$ but affects the “long-range order” structure and the local ordering of the system.

The degree of the “local structural order” on the coexistence curve was analyzed using the Raveché-Mountain-Streett freezing rule.^[36] In accordance with this rule, the ratio of the first non-zero minimum of the RDF $R^{WA} = g_{min}/g_{max}$ was used to calculate the Wendt-Abraham parameter R^{WA} , which characterizes the degree of the “crystallization” or the ordering in a liquid.^[37] In particular, the increase in the value of R^{WA} indicates the decrease of the local structural ordering in a liquid. The values of R^{WA} parameter of argon (insert in Fig. 2a) indicate the presence of structures that are typical for a “dense liquid” on the coexistence curve near the triple point. The values of R^{WA} parameter have a minimum at $T = 90 \text{ K}$, i.e. at this

temperature the structure of the system demonstrates the greatest degree of order. As the triple point of argon is at $T = 83.8 \text{ K}$,^[35] the systems in the vicinity of this point can be viewed as the «dense liquids» with elements of «liquid», which at $T = 90 \text{ K}$ transitions into the equilibrium system with «dense liquid» and «liquid» components. Within this representation we may assume that the systems consist of the “ordered clusters” of argon particles, held together by van der Waals interactions.^[38] The further increase in the temperature leads to the disruption of the equilibrium, disorder in the structure of the system, and the emergence of the “dense liquid-like” component, as indicated by the behavior of the Wendt-Abraham parameter R^{WA} with a pronounced peak at $T = 100 \text{ K}$. Consequently, we can suppose that the increase of the argon temperature between 85 to 110 K leads to multiple repeated changes in its local structure. The greatest local ordering of the studied systems is observed at $T = 100 \text{ K}$. This indicates some slowdown of dynamic processes in the systems under study.

3.2 Dynamic Heterogeneity of Argon on the Coexistence Curve Near the Triple Point

In this research, we primarily focused on specific changes in the kinetic properties of argon near the triple point, the unexpected temporal behavior of which hints at the

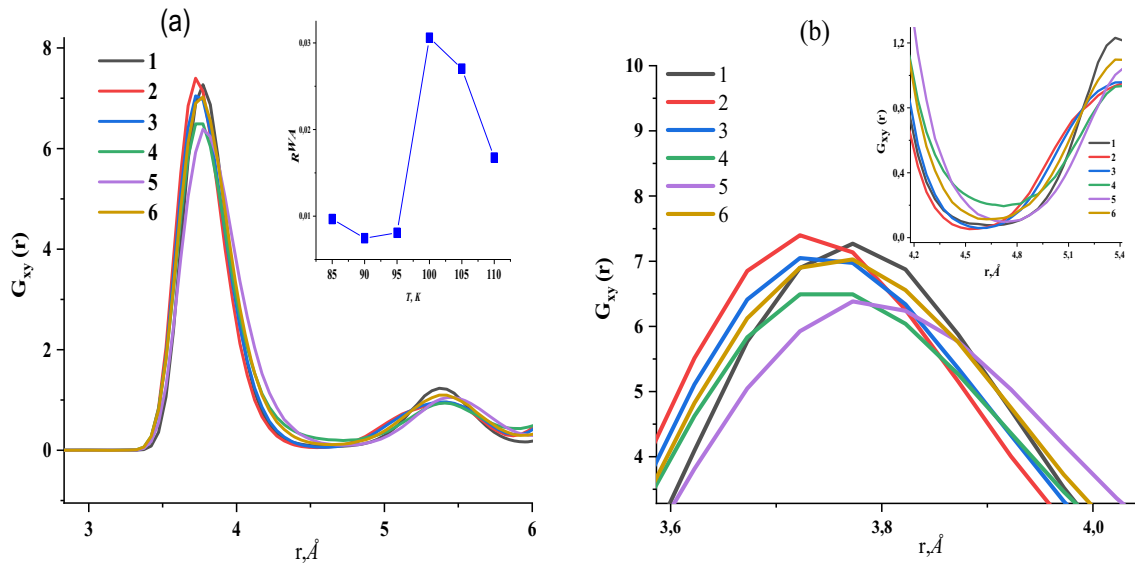


Fig. 2 (a) RDFs $G_{XY}(R)$ between the center of mass of argon at 85 K (1), 90 K (2), 95 K (3), 100 K (4), 105 K (5), and 110 K (6). Inset: R^{WA} parameter of argon (2) at temperatures 85 K (1), 90 K (2), 95 K (3), 100 K (4), 105 K (5), and 110 K (6). (b) Temperature

dependence of the first maximum of $G_{XY}(r)$ at 85 K (1), 90 K (2), 95 K (3), 100 K (4), 105 K (5), and 110 K (6). Inset: temperature dependence of the first minimum of $G_{XY}(r)$ at 85 K (1), 90 K (2), 95 K (3), 100 K (4), 105 K (5), and 110 K (6)

existence of different mechanisms of diffusion at different time scales. A key characteristics that helps to predict the diffusion regimes is the mean-square displacement (MSD) function. The MSD is one of the commonly utilized quantities to characterize the dynamical properties in experiments, theories, and simulations; it can be expressed as^[39]:

$$\langle r^2(t) \rangle = \left\langle \sum_{i=1}^N |\Delta r_i(t)|^2 \right\rangle / N \quad (\text{Eq 3})$$

This function represents the displacement vector of the i -th particle between instants 0 and t . According to Ref 40, 41, MSD describes the kinematic properties of liquids and can be used to determine the self-diffusion coefficient using the Einstein random walk model. The analysis of the MSD time correlation function $\langle r^2(t) \rangle$, as well as the analysis of the parameter α in $\log \langle r^2(t) \rangle \sim \alpha \log t$ function, helps to draw certain conclusions about the motion of argon particles. The value of α reveals the extent to which the diffusion of particles deviates from the Brown diffusion.^[42]

The analysis of the parameter α shows that $\alpha < 1$ for all time intervals at times $t < 250$ ps for all argon systems on the liquid–gas coexistence curves. Consequently, the motion of argon takes place within the framework of the retarded sub-diffusion dynamics.^[41,42]

When studying transitions from one structural phase to another, we studied the mechanisms of motion of the selected “tracker” argon. This argon can be viewed as a kind of defect in the “new” structure of argon when

changing the physical characteristics of the system. The motion of argon particles leads to the change in the local structure of the “new” argon system, resulting in the change in the diffusion mechanisms in argon not only during the changes in the physical characteristics of the system but also at different time intervals.

MSD analysis at different time intervals was performed with the help of Frenkel theory and the V–T theory, which is based on the many-body Hamiltonian formulation,^[43,44] and which is applicable for the description of the dynamic properties of liquids. Considering the Frenkel’s theory^[45] and V–T formalism applied to the description of the particles’ motion in liquid,^[46,47] MSD $\langle r^2(t) \rangle$ function can be represented as follows^[48]:

$$\langle r^2(t) \rangle = \langle r^2(t) \rangle_{\text{vib-jump}} + \langle r^2(t) \rangle_{\text{tr}} + \langle r^2(t) \rangle_{\text{rw}} \quad (\text{Eq 4})$$

The diffusion interval at $0 < t_D$ is the time interval within which the motion can be described within different frameworks of the diffusion model representations. In this interval $0 < t_D$ the following sub-intervals can be distinguished: $\langle r^2(t) \rangle_{\text{vib-jump}}$ the time scale that corresponds to the vibrational-hopping diffusion; $\langle r^2(t) \rangle_{\text{tr}}$ determines the crossover interval of diffusion at $t_D < t_{RW}$. The $\langle r^2(t) \rangle_{\text{rw}}$ interval determines the transit random walk interval t_{RW} , within which the particle participates in the collective motion of the liquid. In our case t_{RW} is the time at which $\langle r^2(t) \rangle$ corresponds to the sub-diffused retarded motion of the “tracking” particle of argon in the collective motion of the particles in the system. The t_D denotes the time when

$\langle r^2(t) \rangle$ deviates from $\langle r^2(t) \rangle_{\text{vib-jump}}$, as $\langle r^2(t) \rangle_{\text{vib-jump}}$ interval only describes the vibrational-hopping mechanism of diffusion. In the first approximation,^[45,46] diffusion

processes in each time interval can be described within frameworks of the respective model representations, whose existence confirms the assumption of the system's temporal dynamics heterogeneity.

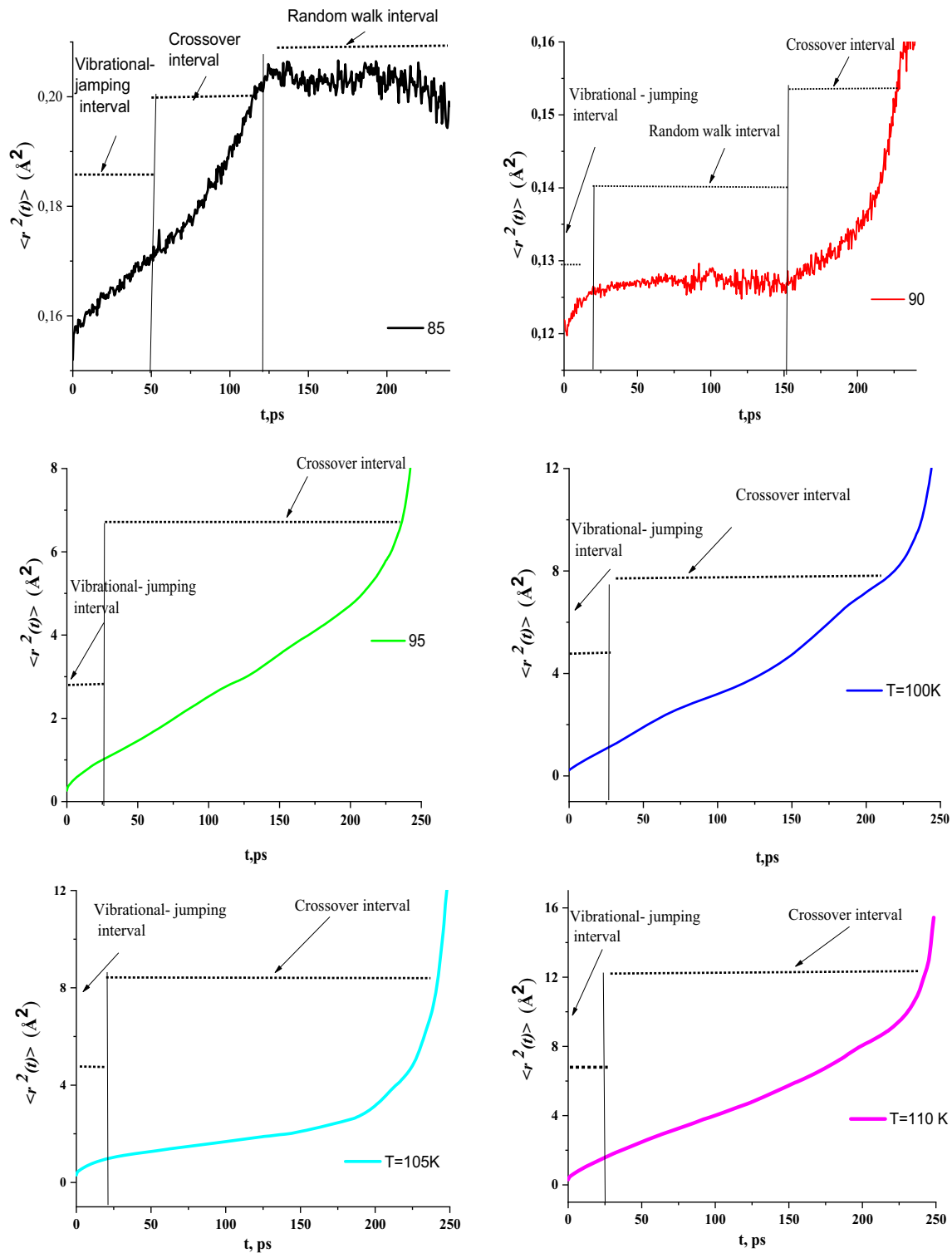


Fig. 3 MSD of the center of mass of argon on the coexistence curve near the triple point at temperatures 85 K (1), 90 K (2), 95 K (3), 100 K (4), 105 K (5), and 110 K (6)

During the analysis of the $\langle r^2(t) \rangle$ function (Fig. 3), we should note that at all temperatures the $\langle r^2(t) \rangle_{\text{vib-jump}}$ interval is bound by time of approximately ~ 25 ps.

In other words, for this time interval the diffusion of argon on the coexistence curve can be described within the framework of Frenkel's model representation, that is, argon undergoes vibrational motion around the equilibrium position with a subsequent jump by an interparticle distance into the next equilibrium position.

At $T = 85$ K a crossover interval is observed for $25 \text{ ps} < t < 120 \text{ ps}$, corresponding to the diffuse regime of particles' motion; for $t > 120 \text{ ps}$ argon moves in a retarded sub-diffuse regime. At $t > 120 \text{ ps}$ and at $T = 85$ K is the time when transit random walk became a stationary process. The reason why the motion of argon slows down can be attributed both to the change in the local structure of the "dense liquids" and the collective motion of the argon particles. At the same time, the particles in the system transition from the "dense liquids-like" to a "liquid-like" motion regime.

At $T = 90$ K the change in the local structure of liquid continues, as indicated by the presence of the random walk interval on $\langle r^2(t) \rangle$ at times between 25 and 150 ps. The time dependencies of $\langle r^2(t) \rangle$ within which two diffusion regimes exist (vibrational-hopping interval, crossover interval) are observed for systems of the second group at $T > 90$ K. In this group, the random walk interval is noticeably absent due to the increase in the impact of the «liquid-like» motion of argon.

The result obtained does not correlate with the conclusions of the authors of the work,^[38] who state that in "dense liquids (near the triple point) there is no empty space so that one molecule can move or turn in it. Therefore, a single molecule can only move together with other molecules, as part of some collective." Our results partially refute the conclusions of the authors of the work:

Namely, we have found that the mechanism of motion of an individual argon molecule near the critical point at $85 \text{ K} < T < 90 \text{ K}$ at short times $t < 25 \text{ ps}$ can be described in terms of vibrational-hopping diffusion, which describes the motion of an individual argon molecule, i.e. molecules move independently in a liquid for short times. An increase in temperature on the coexistence curve leads to a decrease in the duration of the interval of vibrational hopping diffusion.

Only under certain physical conditions (in our case, at $T = 85 \text{ K}$ and $T = 90 \text{ K}$), the argon molecule takes part in joint motion in the composition of complexes only at $t > 120 \text{ ps}$ and for 100 ps. In this time interval, due to the VDW interaction, the formation of joint complexes of argon molecules occurs, which is confirmed by the conclusions of the work^[38] a change in the mode of motion in

the system, as evidenced by the presence of a crossover interval.

These results indicate that at $T < 90 \text{ K}$, the models describing motion in terms of representing motion in a "dense liquid" are more correct. The "dense liquid-like" to "liquid-like" transition takes place at $T \sim 90 \text{ K}$.

At $T > 95 \text{ K}$ the crossover interval has almost the same duration. This may indicate that at $T > 95 \text{ K}$ a qualitative change in the motion of the system's component takes place: in particular, the "liquid-like" sub-diffuse mechanism of motion of particles in the liquid begins to dominate.

As the temperature range of the system with $85 \text{ K} < T < 90 \text{ K}$ is close to the triple point "the anomalous-normal crossover dynamics can be extended to a crossover from slower to faster sub-diffusion. In such approach, the crossover between different diffusion regimes thus naturally emerges, and the type of tempering governs the exact crossover shape"^[49]. In such case, according to Frenkel,^[45] the intermolecular interaction in the argon system near the triple point can be viewed as the interaction in the "dense liquid"^[50]. At the same time, according to the results of Ref 51, the diffusion processes in the systems are determined by the activation jumps of the liquid particles (the vibrational-hopping mechanism). As the triple point of argon is at $T = 87.3 \text{ K}$, we can expect that near this point at $T < 90 \text{ K}$ the interaction energy between the particles is high enough to make methods used to study argon systems applicable in our research. At the same time, we can expect that between the jumps, argon particles undergo vibrational motion around their equilibrium positions. When undergoing such motion, the argon system can be considered as an almost harmonic oscillatory system with rather rare particle jumps. According to Frenkel,^[45] at a temperature close to the melting temperature ($T = 83.6 \text{ K}$ ^[52]), the characteristic time τ_0 between jumps of argon over distances comparable to inter-particle distance significantly exceeds the shortest time of the particle's oscillation period $\tau_0 = \frac{2\pi}{\omega_0}$, where ω_0 is the maximum frequency of acoustic disturbances in the system (of the Debye frequency order).

Based on the dynamic characteristics of the system on the coexistence curve near the triple point at times $t < 25 \text{ ps}$, it can be treated as a practically harmonic vibrational system with isolated rare particle jumps. It should also be noted that at a temperature near the triple point the characteristic values of the diffusion coefficient corresponding to the jumps of the particle are comparable to the time of one fluctuation of τ_0 . The average jump time by an inter-particle distance is determined by the expression for the self-diffusion coefficient $\tau = \frac{a^2}{6D}$,^[51] where a —the average distance between particles, obtained from RDF analysis (Fig. 2).

The effective van der Waals radius of the argon modeled as spheres is $R^{\text{argon}} \sim 1.79 \text{ \AA}$.^[55] Thus, based on the RDFs analysis of the first maximum, the value of the smallest distance between the interacting particles is $\sim 3.8 \text{ \AA}$.

An average value of the self-diffusion coefficient can be calculated by integration over the velocity autocorrelation function (VAF) defined as $Z(t) = \frac{1}{3} \langle \vec{v}(0) \vec{v}(t) \rangle = \langle v_x(0) v_x(t) \rangle$ ^[32]:

$$D_s = \frac{1}{3} \int_0^\infty \langle \vec{v}(0) \vec{v}(t) \rangle dt \tag{Eq 5}$$

The D_{Ar} values (Fig. 4) obtained at $T = 85$ and $T = 110 \text{ K}$ correlate quite well with the argon diffusion coefficient D_{Ar} of argon presented in Ref 53, 54. Thus, the change in the temperature of the argon system on the coexistence curve near the critical point is likely to lead to a non-monotonous dependence of the average jump time by an inter-particle distance on the temperature. A significant decrease in the average jump time by an inter-particle distance is closely related to the change in its local structure and the impact of the “liquids-like” component of the system on its overall dynamics. Taking into account the results of Ref 51, the jump time τ_0 (Fig. 4) near the triple point can be viewed as the relaxation time of the system. The values of τ_0 we obtained at $T = 85 \text{ K}$ correlate rather well with the relaxation time of the argon system described in Ref 56. The difference between these values can be attributed to the choice of the calculation methods. We have demonstrated that the change in the temperature of the argon system on the coexistence curve near the critical point leads to a non-monotonous dependence of relaxation time on the temperature. A significant decrease in the time of relaxation of the system is closely related to the change in its local structure and the impact of the “fluid-like” component of the system on its overall dynamics. The

temperature dependence of the jump time τ_0 (Fig. 4) reaches a maximally deviates from the monotonic dependence at $T = 95 \text{ K}$, indicating the acceleration of the motion of the particles at this temperature and the qualitative change in the mechanism of diffusion, further supporting the idea that at this temperature there is a transition from a “dense liquid” to a “liquid structure”, which is reflected in a fundamental change in the dynamics of the system at times greater than 25 ps and of the impact of the “liquid like” component of the system on its overall dynamics.

4 Conclusions

The paper presents a methodology developed on the basis of V–T theory, phonon theory of liquid, and Frenkel’s approaches, which makes it possible to determine: the exact temperature and pressure values at which the transition from “dense liquid” to less dense “liquid” occurs on the “liquid–vapor” coexistence curve; for each T–R state on the “liquid–gas” coexistence curve, determine the presence and duration of time intervals within which the components of the liquid take part in a single movement or move as part of joint complexes;

The developed methodology was used to study the structural-dynamic properties near the triple point of argon on the liquid-vapor coexistence curve. We have shown that at short times less than 25 ps, regardless of the T–P state of the system, the mechanisms of argon motion can be described in terms of vibrational-hopping diffusion.

We also have demonstrated that near the triple point argon, two temperature intervals exist in each of which the dynamic behavior of argon is significantly different: these are a low-temperature interval with $T < 90 \text{ K}$ and a high-

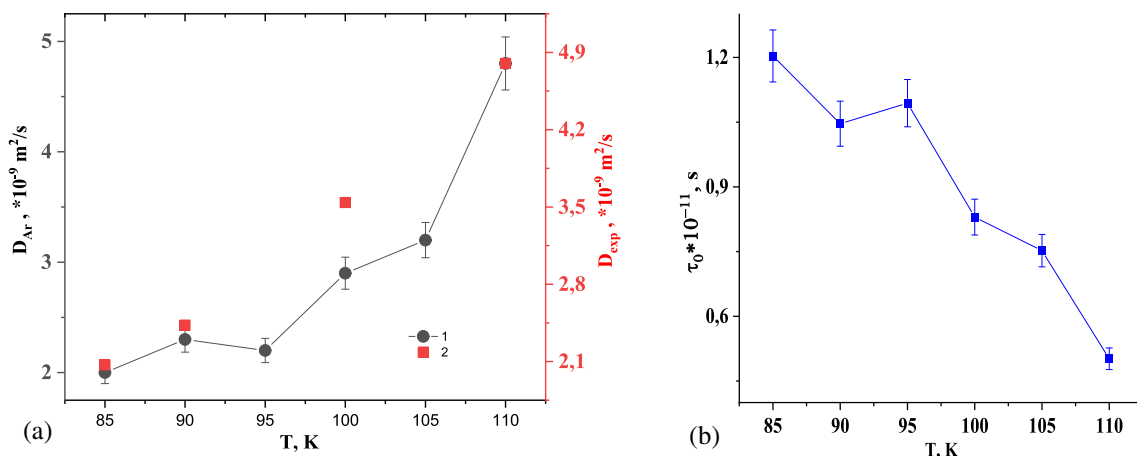


Fig. 4 Temperature dependence of: (a) diffusion coefficient of argon D_{Ar} (1) from MD calculation, (2) from Ref. 53, 54; (b) τ_0 jump time by an interparticle distance on the coexistence curve at temperatures 85 K (1), 90 K (2), 95 K (3), 100 K (4), 105 K (5), and 110 K (6)

temperature interval at $T > 90$ K. The motion of argon at $T < 90$ K can be described within the framework of a «dense liquid». At increasing temperatures, the change in the local structure with a gradual transition from the «dense-liquid» to «liquid-like» motion of particles in the system occurs. The dynamics of argon at $T > 90$ K is characterized by the absence of the transit random walk interval, indicating the increasing role of the «liquid-like» with «gas-like» component in the liquid's dynamics.

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