



Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: [www.elsevier.com/locate/molliq](http://www.elsevier.com/locate/molliq)

## Specific properties of argon-like liquids near their spinodals

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### ARTICLE INFO

#### Article history:

Received 17 August 2016

Received in revised form 21 December 2016

Accepted 23 January 2017

Available online xxxx

#### Keywords:

Noble gases

Self-diffusion coefficient

Kinematic shear viscosity

Maxwell relaxation time

Isochoric compressibility

Spinodal

### ABSTRACT

The work is devoted to the computer simulation study of the spinodal position for argon and low-molecular liquids having the averaged interparticle potentials similar to that for argon. For this purpose several new methods are developed: the study of the intersection points for pressure curves on pairs of two close isochors, specific changes for the isochoric behavior of the radial correlation functions near the spinodal, non-trivial changes of the temperature dependencies for isochoric values of the self-diffusion coefficient, kinematic shear viscosity and Maxwell relaxation time of argon at the intersection of its spinodal. The three last characteristics are determined with the help of analysis of long time tails for the velocity auto-correlation function. Obtained in such a way the position of spinodal is compared with that following from the experimental study and computer simulations of the isothermal compressibility.

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### 1. Introduction

Thermodynamic properties of metastable states and the determination of their boundaries are studied in many works (see [1–18]). An interest to this problem is explained by the interaction specificity of high energy electromagnetic radiation with substance [1], shock action phenomena in condensed matter [2] as well as some practical problems connected with storage safety of liquation gases [3,4].

The computer simulation methods are often used for the study of metastable states [5–10,18] since homogeneous phases are problematically realized far of binodal. Among works devoted to the study of liquid properties in the vicinity of spinodal it is necessary to pick out [5–7] devoted to the dynamics of sizes for heterogeneous fluctuations in one and two-component liquids described with the help of the Lifshits-Slezov theory, as well as the works [8–18] devoted to the direct determination of thermodynamic stability boundaries. Theoretical results in [11–16] are based on the decision of the corresponding equations of state. At the same time, it is noted in [12] that the applicability of the lasts is strongly restricted in metastable range.

The position of spinodal is determined in [8–10] from the analysis of the density dependence for the tangential component of the pressure tensor. For this aim the properties of thin layer of liquid phase contacting with gaseous phase are investigated. The spinodal density is determined as that corresponding to the maximal value of tangential

component for the pressure tensor. The position of spinodal in [17] is studied by experimental method: it is taken into account that the low frequency sound velocity tends to zero for all spinodal points. In [18] the molecular dynamics methods are attracted in order to determine the stability boundary for liquid and crystalline argon. These points correspond to minimum points (in the pressure-density coordinates) on isotherms extrapolated to the metastable region.

Here it is necessary to note that the spinodal is usually considered as the separatrix between absolutely unstable states and stable and metastable ones. Such a division of possible states of a system is only correct in the thermodynamic limit, i.e. for quasi-static processes. At the same time the existence of the range of absolutely unstable states should manifest itself also in kinetic processes with characteristic times essentially more than those for molecular processes. The different manifestation of the spinodal in frequency dependence of the longitudinal sound velocity can serve as a typical example of said above. From this point of view, the analysis of the self-diffusion coefficient and kinematic shear viscosity seems to us to be the most perspective for the establishment of the spinodal position.

In the present paper our main attention is focused on specific changes of the kinetic coefficients near the spinodal. In the first place we have in view the self-diffusion coefficient, kinematic shear viscosity and Maxwell relaxation time for shear tensions. These quantities are determined with the help of long-time tails of the velocity auto-correlation function (VACF) for a molecule. Our calculations are mainly carried out for argon. However, the main results can be also applied for other low-molecular liquids for which the averaged intermolecular potentials have argon-

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like character. This circumstance is illustrated on the example of liquid nitrogen.

## 2. The calculation methods

### 2.1. Calculation procedure

In the present paper our main attention is focused on specific changes of the kinetic coefficients near the spinodal. In the first place we have in view the self-diffusion coefficient, kinematic shear viscosity and Maxwell relaxation time for shear tensions. These quantities are determined with the help of long-time tails of the VACF for a molecule. In turn, the VACF of a molecule is modeled on isochors with the help of computer simulations. We suppose that the interparticle interaction is described by the standard Lennard-Jones potential:

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

$$\frac{\epsilon}{k_B} = 119.5 \text{ K}, \quad \sigma = 3.405 \text{ \AA}$$

where  $k_B$  is the Boltzmann constant. The cutoff radius for the potential is accepted to be equal:  $r_c = 7.5\sigma$ .

For molecular dynamic (MD) simulations we consider NVE ensemble consisting from  $50^3 = 125000$  atoms of argon which occupy the cubic cell with the linear size  $l_1 = 18.02$  nm (at the temperature  $T = 83.815$  K) close to the triple point of argon. The periodic boundary conditions are used. To test the influence of the size of NVE ensemble we compare our results of kinetic coefficients calculations with those corresponding to the NVE ensemble of  $10^6$  particles with  $l_1 = 36$  nm. The results are identical so the interference effects due to periodic boundary conditions are negligible. The model is satisfy the requirements formulated in [19]. The Gromacs 5.01 software environment [20,21] was used for our purposes.

It will be shown that all enumerated kinetic coefficients have characteristic peculiarities near the spinodal.

It is necessary to note that the self-diffusion coefficient is determined in the standard way [22]:

$$D_s(T) = \frac{1}{3} \int_0^\infty \varphi_{\bar{v}}(t) dt \quad (1)$$

where  $\varphi_{\bar{v}}(t)$  is the VACF of a molecule, and with a help of the equation  $\Gamma(t) = C + 6D_s t$ , where  $\Gamma(t)$  is the mean square displacement of a molecule. The numerical method will be correct if both obtained values of the self-diffusion coefficients are identical [19,22]. It is one of main criteria for our calculation.

At the same time for the determination of the kinematic shear viscosity and the Maxwell relaxation time we use the long-time asymptote of the VACF [23]:

$$\varphi_{\bar{v}}(t) \underset{t \rightarrow \infty}{\approx} \frac{2k_B T}{\rho [4\pi\nu t]^{3/2}} \left( 1 - \frac{15}{4} \frac{\tau_M}{t} + \dots \right) \quad (2)$$

where  $T$  and  $\rho$  are temperature and mass density correspondingly,  $\nu$  is the kinematic shear viscosity and  $\tau_M$  is the Maxwell relaxation time. In connection with this the kinematic shear viscosity and the Maxwell relaxation time are determined by the relations:

$$\nu(T) \underset{t \rightarrow \infty}{=} \frac{1}{4\pi A(t)t}, \quad A(t) = \left( \frac{\varphi_{\bar{v}}(t)\rho}{2k_B T} \right)^{2/3} \quad (3)$$

$$\tau_M(T) \underset{t \rightarrow \infty}{=} \frac{2}{5} t(1 - 4\pi\nu A(t)t) \quad (4)$$

Analyzing the behavior of  $D_s$ ,  $\nu$  and  $\tau_M$  on isochors we develop three independent methods for the determination of the spinodal position.

Besides, we will study the peculiarities of the density correlations near the spinodal. More exactly, we will show that the character of decrease for the radial distribution function  $g(r)$  on isochore is different above and below spinodal. This circumstance can be used as one more method for the determination of the spinodal position. In addition to this we will investigate the temperature dependence of the pressure on isochors:

$$p(n, T) = nk_B T - \frac{2}{3} \pi n^2 \int_0^\infty r^3 \Phi'(r) g(r) dr \quad (5)$$

where  $n$  is the particle number density. It will be shown that the temperature dependencies of pressure on two close isochors intersect at some point, which belongs also to the spinodal. We will ascertain that all different methods indicated above are consistent that increases the confidence to each of them.

It is supposed that temperature dependencies of all indicated characteristics of a system are sensible to the transfer from stable or metastable states to absolutely unstable ones, i.e. to the transfer taking place on the spinodal. At the same time, it is expected that the transfer from stable to metastable states, taking place on the binodal, is characterized by more weakly expressed peculiarities.

### 2.2. Qualitative analysis of the self-diffusion on isochors

In this Section we want to discuss the causes of peculiarities for different kinetic and thermodynamic characteristics of a system arising at the intersection of the spinodal.

For this aim let us discuss the behavior of the self-diffusion coefficient of argon on its isochors. In accordance with dimensional reasons the self-diffusion coefficient of argon has the structure:

$$D_s = \kappa_D \frac{k_B T}{\eta r_p} \quad (6)$$

where  $\eta$  is the dynamic shear viscosity and  $r_p$  is the effective radius of a molecule. The proportionality coefficient  $\kappa_D$  is equal to  $\frac{1}{6\pi}$  for the spherical coarse particles [22]. The shear viscosity on isochors is practically independent on temperature [25], therefore for the self-diffusion coefficient we can write:

$$D_s = d(n)T, \quad d(n) = \kappa_D \frac{k_B}{\eta(n)r_p} \quad (7)$$

If the temperature decreases below the spinodal one, the system delaminates on vapor and liquid phases. In this case we have:

$$D_s = \zeta_D(T) D_s^{(V)} + (1 - \zeta_D(T)) D_s^{(L)} \quad (8)$$

where  $\zeta_D(T)$  is the fraction volume occupied by the vapor phase,  $D_s^{(V)}$  and  $D_s^{(L)}$  are the self-diffusion coefficients in the points of intersections of the vapor and liquid isochors with the spinodal at given temperature:

$$D_s^{(L)} = d(n_s^{(L)}(T))T \text{ and } D_s^{(V)} = d(n_s^{(V)}(T))T \quad (9)$$

Here it is necessary to note that  $d(n_s^{(V)}(T))$  will be also represented in the form Eq. (7).

Substituting Eq. (9) in Eq. (8) we obtain:

$$D_s(T) = D_s^{(L)}(T) + \zeta_D(T) (d_s^{(V)} - d_s^{(L)})T \quad (10)$$

where  $d_s^{(L)} = d(n_s^{(L)}(T))$  and  $d_s^{(V)} = d(n_s^{(V)}(T))$ . Since  $d_s^{(V)} > d_s^{(L)}$ , the slope angle of the self-diffusion line below spinodal is expected to be more than that over spinodal. The self-diffusion curve is continuous on the spinodal.

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