STUDY OF THE FUNCTIONAL FORM OF INTERMOLECULAR POTENTIAL ON THE BASIS OF SELF-DIFFUSION OF LIQUID MOLECULES

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On the basis of researches of the temperature dependence of one-particle contributions to the self-diffusion coefficient, the fitting values of the slope parameter of the potential function have been calculated. The theoretical values of the self-diffusion coefficient of liquid argon coincide with both experimental data and the results of a computer simulation obtained at certain values of the slope parameter, with the auto-correlation function of the molecular velocity being approximated best by a quadratic polynomial.

According to the general theory [1—5], the self-diffusion coefficient D is presented as a sum

$$D = D_1 + D_c,$$

of the collective, D_c, and one-particle, D_1, components. The algorithm of calculations of the collective component was described in detail in work [6], while some numerical estimations of this parameter for different liquids were obtained in work [7]. At the same time, the one-particle component of the self-diffusion coefficient is not studied sufficiently; in fact, we know a single work dealing with this issue [8].

An important stage in studying the diffusive processes is a correct account of intermolecular interactions, based on the proper choice of an adequate model form of the intermolecular potential. On the other hand, the potential function can be reproduced making use of the self-diffusion experimental data and comparing them with theoretical calculations, as it is done, for example, when calculating the effective pair potential from the known radial distribution function [9] or when constructing an authentic potential curve of intermolecular interactions on the basis of the method of inverse scattering transform [10].

In this work, we have studied the correlation between the one-particle component of the self-diffusion coefficient and the repulsive part of a model intermolecular potential and, by fitting the theoretical value of a certain parameter to the corresponding experimental data, the value of this parameter has been determined.

The character of the decrease of the one-particle contribution to the molecule-velocity autocorrelation function (MVACF) at small times is governed by the behavior of repulsive forces at distances shorter than the molecule diameter. Really, at small times, the MVACF is determined by the expansion series

$$\langle \bar{v}(t)\bar{v}(0) \rangle = \langle \bar{v}^2(0)) \rangle + \langle \bar{v}''(0)\bar{v}(0) \rangle \frac{t^2}{2} + \dots, \qquad (1)$$

where $v(t)$ is the velocity of a selected liquid molecule. In agreement with the results of work [11], the expression for the autocorrelation function at small t can be written down as

$$\varphi(t) = \varphi_1(t) = \frac{3kT}{M} \left(1 - \frac{1}{2} \frac{t^2}{\tau_0^2} + \dots \right), \qquad (2)$$

where k is the Boltzmann constant, T is the absolute temperature, M is the molecule mass, and

$$\tau_0^{-2} = \frac{\langle \Delta U(\bar{r}) \rangle}{3M}, \qquad (3)$$

or, approximately,

$$\varphi_1(t) \approx \frac{3kT}{M} \exp\left(-\frac{1}{2} \frac{t^2}{\tau_0^2} \right). \qquad (4)$$

For the numerical evaluation of τ_0, we use a spherically symmetric intermolecular potential in the form

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^m - \left(\frac{\sigma}{r} \right)^6 \right], \qquad (5)$$

whence we obtain the following expression for $\Delta U(r)$:

$$\Delta U(r) = \frac{4\varepsilon}{\sigma^2} \left[m(m+1) \left(\frac{\sigma}{r} \right)^{m+2} - 42 \left(\frac{\sigma}{r} \right)^8 \right]. \qquad (6)$$
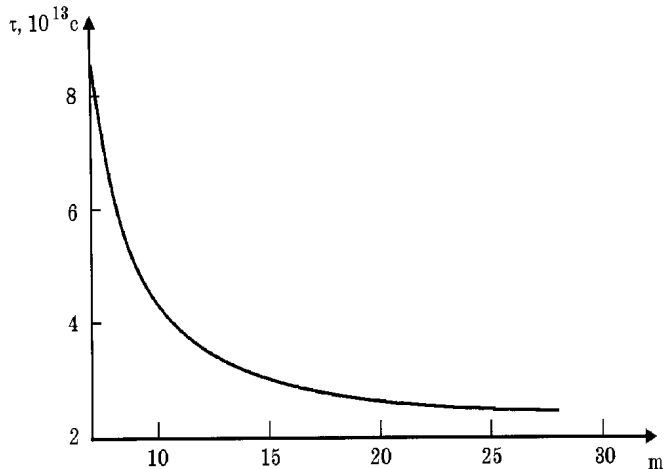
Fig. 1. Dependence of τ_0 on the slope parameter m

Using expressions (3) and (6) and the mean field approximation, where

$$\left\langle \left(\frac{\sigma}{r}\right)^m \right\rangle \approx \left(\frac{\sigma}{\langle r \rangle}\right)^m \approx \left(n\sigma^3\right)^{m/3}, \qquad (7)$$

we obtain

$$\tau_0^{-2} = \frac{4\varepsilon}{3M\sigma^2}\left[m(m+1)\left(n\sigma^3\right)^{(m+2)/3} - 42\left(n\sigma^3\right)^{8/3}\right]. \qquad (8)$$

Fig. 1 shows the dependence of τ_0 on the slope parameter of repulsive forces m at the temperature $T = 100$ K. For example, at $m = 12$ which corresponds to the Lennard–Jones potential, the decay time of the MVACF turns out equal to 3.55×10^{-13} s. A comparison of the results of computer simulation [8] with the normalized autocorrelation functions $\tilde{\varphi}_1(t) = \frac{M}{3kT}\varphi_1(T)$ calculated according to formulae (2) and (4) is presented in Fig. 2. The calculations were carried out for the values of the slope parameter $m = 18$ and 24 on the isotherm $T = 100$ K. As is seen from Fig. 2, the dependence of the normalized autocorrelation function of the one-particle contribution $\tilde{\varphi}_1(t)$, which decays by the polynomial law, intersects the data of molecular dynamics [8] at a definite point $x_* = \frac{t}{2\tau_M} = 0.78$, if the slope parameter $m = 24$, where τ_M is the Maxwell relaxation time of viscous stresses in the liquid. Thus, summing up both plots, the MVACF can be written down as

$$\varphi(t) = [\varphi_1(t) - \varphi_c(t)]\theta(t_* - t) + \varphi_c(t), \qquad (9)$$

where

$$\begin{cases} \theta(t_* - t) = 0, & t_* - t < 0, \\ \theta(t_* - t) = 1, & t_* - t > 0, \end{cases}$$
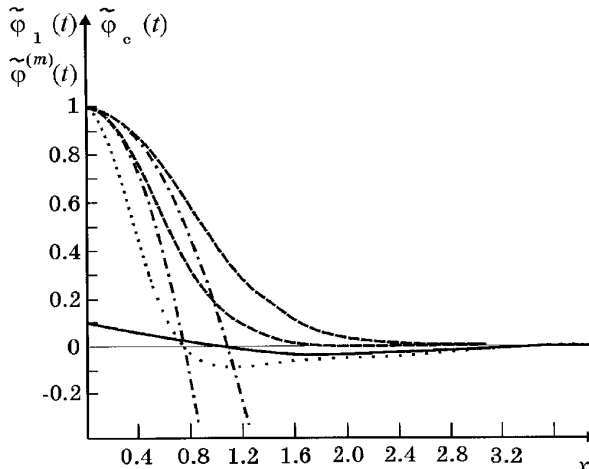

Fig. 2. Time dependences of the autocorrelation functions. The solid curve corresponds to the normalized autocorrelation function of a Lagrange particle [5], the dash-dotted curves to the dependences $\tilde{\varphi}_1(t)$ that decay by a polynomial law, the dashed curves to exponential dependences, and the dotted curve to a dependence obtained on the basis of the molecular dynamics data [8]

$\varphi_c(t)$ is the collective component of the MVACF, and $t_* = 2\tau_M x_*$. In accordance with formula (9), the one-particle contribution to the self-diffusion coefficient of a molecule is determined by the expression

$$D_1 = \frac{1}{3}\int_0^{t_*} [\varphi_1(t) - \varphi_c(t)]dt. \qquad (10)$$

The values of the self-diffusion coefficient D of liquid argon, taking into account formula (10), are quoted in the table. In this table, the notation D_P is used for the self-diffusion coefficient calculated taking into account the dependence $\tilde{\varphi}_1(t)$ in the form of a quadratic polynomial, D_G in the case of the Gaussian exponent dependence, and $D_{\exp}$ for the experimental value of the self-diffusion coefficient [12]. The best agreement between theoretical values and experimental data takes

Self-diffusion coefficient of liquid argon at $T=100$ K for various values of the slope parameter m

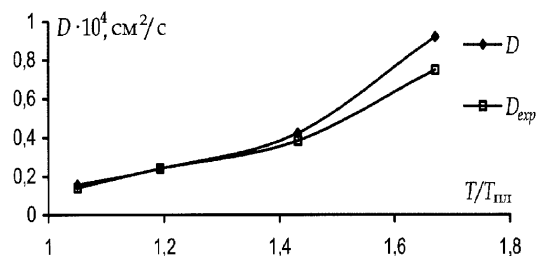| m	$t_* \times 10^{13}$, s	$D_G \times 10^5$, cm^2/s	$D_P \times 10^5$, cm^2/s	$D_{\exp} \times 10^5$, cm^2/s
28	3.44	2.54	2.395	
24	3.47	2.61	2.416	2.47
18	3.81	2.72	2.61	
12	5.03	3.17	3.298	

Fig. 3. Comparison of theoretical and experimental [12] temperature dependences of the self-diffusion coefficient of liquid argon. T_m is the melting temperature

place for the slope parameter values $m = 24$ and 28. A comparison of the theoretically calculated temperature dependence of the self-diffusion coefficient with experimental data [12] is presented in Fig. 3.

We note that the computer simulation of the MVACF, carried out making use of the Lennard–Jones potential (12:6), resulted in a more abrupt decay of this function in comparison with the polynomial dependence (4). Moreover, formula (4) reproduces the results of computer simulation [12], obtained for the slope parameter values of 24 and 28, with quite a good accuracy, which is in a qualitative agreement with the results obtained in work [13], where the slope parameter values were obtained on the basis of the analysis of the statistically substantiated equation of state.

Summarizing the results reported in this work and taking into account the results of works [13, 14], we may say that the slope of the potential function is an individual characteristic of the specific substance considered in the framework of the power-law model of intermolecular potential, and the value of this parameter depends on the aggregate state of the substance (for example, for gaseous argon, $m \approx 15$ [14]). Thus, all those circumstances evidence for an effective character of the functional form of the repulsive potential.

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ДОСЛІДЖЕННЯ ФУНКЦІОНАЛЬНОЇ ФОРМИ
МІЖМОЛЕКУЛЯРНОГО ПОТЕНЦІАЛУ
НА ОСНОВІ САМОДИФУЗІЇ
МОЛЕКУЛ РІДИНИ

В.Ю.Бардик, К.С.Шакун

Р е з ю м е

На основі дослідження температурної залежності одночастинкових внесків у коефіцієнт самодифузії обчислено підгінні значення параметра крутизни потенціальної функції. Теоретичні значення коефіцієнта самодифузії для рідкого аргону збігаються з експериментальними даними та результатами машинного моделювання при певних значеннях параметра крутизни. При цьому автокореляційна функція швидкості молекули найбільш вдало апроксимується квадратичним поліномом.