LIQUIDS AND LIQUID CRYSTALS

INFLUENCE OF PRESSURE ON COLLECTIVE TRANSPORT IN SIMPLE LIQUIDS

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The values of the effective diameter of a molecule are calculated within the model of hard spheres with the use of the Carnahan–Starling equation of state, basing on the analysis of the data on the molecular dynamics of the self-diffusion of liquid argon. It is shown that the contribution of the collective component of the self-diffusion coefficient in the high-pressure range amounts approximately to 76%.

In the general case, the heat motion in liquids represents a combination of shifts of molecules with respect to their nearest surrounding and the collective drift in the field of thermal hydrodynamic fluctuations [1, 2]. It follows from physical considerations that an increase of the pressure which is accompanied by the growth of the liquid density results in the essential increase of the relative role of the collective component of the self-diffusion coefficient. Indeed, due to the geometric restrictions, the relative
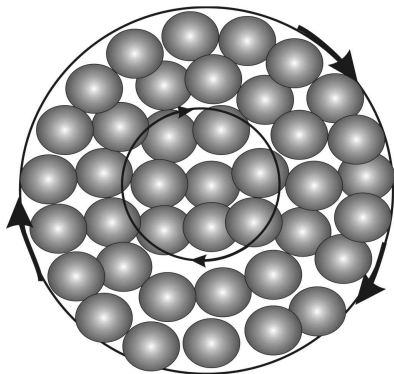

Fig. 1. Thermal displacements of molecules in a compressed fluid due to the appearance of thermal vortex excitations

motion of molecules is increasingly reduced to oscillations in the cell formed by the nearest neighbors. At the same time, an increase in the liquid density influences the vortex modes of the heat motion of molecules to a much smaller extent (Fig. 1). Since the collective transport in a liquid is related just to vortex (transversal) modes, this allows one to conclude about the increasing role of the collective component of the self-diffusion coefficient as the pressure grows.

It is worth noting that an increase of the degree of "collectivization" of the molecular motion affects, in some way, the self-diffusion and the shear viscosity and takes place in associated liquids. That is why it is appropriate to consider, first of all, the influence of the pressure on the processes of self-diffusion in simple liquids, in particular, in liquid argon.

In correspondence with the data of works [1,2], the self-diffusion coefficient of liquid molecules can be presented in the form

$$D = D_{\mathrm{col}} + D_r, \tag{1}$$

where D_{col} and D_r stand for the collective and single-particle contributions, respectively. The collective component of the self-diffusion coefficient is related to the temperature T, dynamic η and kinematic ν shear viscosities, as well as the Maxwellian time of relaxation τ_{M} of the transversal modes by the formula

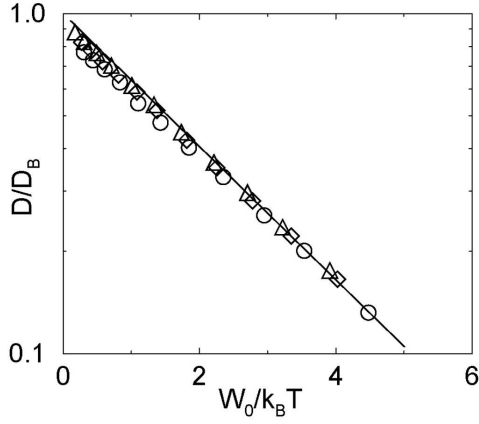$$D_{\mathrm{col}} = \frac{k_{\mathrm{B}}T}{10\pi\eta\sqrt{\nu\tau_{\mathrm{M}}}}. \tag{2}$$

Fig. 2. Dependence of the scaled self-diffusion coefficient of argon on the dimensionless combination $W_0/k_{\mathrm{B}}T$ ($\circ$ – $T = 298$ K, $\diamond$ – $T = 1000$ K, and $\triangle$ – $T = 3000$ K) [3]

The dependence of the Maxwellian relaxation time on the shear viscosity of the medium is approximated by the expression [1,2]

$$\tau_{\mathrm{M}} = \tau_{\mathrm{M}}^0 \left(\frac{\nu}{\nu_0}\right)^{2/3}, \tag{3}$$

where $\nu_0 = 0.00134$ cm^2/s and $\tau_{\mathrm{M}}^0 = 2.22 \times 10^{-13}$ s are the values of the corresponding parameters at a temperature of 100 K [1,2].

The behavior of the self-diffusion and viscosity coefficients of liquid argon during the increase of the external pressure in the interval (1.3–52) GPa was an object of the molecular-dynamic investigation performed in [3]. The molecular motion was simulated as a motion of spheres characterized by the Buckingham potential of intermolecular interaction

$$U(r) = \varepsilon \left(A e^{-\alpha \frac{r}{r_0}} - B \left(\frac{r_0}{r}\right)^6\right), \tag{4}$$

where $A = \frac{6e^{\alpha}}{\alpha - 6}$ and $B = \frac{\alpha}{\alpha - 6}$. The parameters of the potential have the following values: $\frac{\varepsilon}{k_{\mathrm{B}}} = 122$ K, $r_0 = 3.85$ Å, $\alpha = 13.2$. The densities of the investigated system lie within the limits from ≈ 0.6 g/cm^3 to 1.95 g/cm^3 (at $T = 298$ K, $P = 1.3$ GPa), to 2.75 g/cm^3 (at $T = 1000$ K, $P = 9.3$ GPa), and to 4.05 g/cm^3 (at $T = 3000$ K, $P = 52$ GPa). For the sake of obviousness, Figs. 2 and 3 present the graphs of the data of a model experiment from [3]. The quantities D_{B} and η_{B} denote the Boltzmann coefficients of self-diffusion and viscosity determined by the expressions [4]

$$D_{\mathrm{B}} = 1.019 \frac{3}{8n\sigma^2} \left(\frac{k_{\mathrm{B}}T}{\pi m}\right)^{1/2}, \tag{5}$$
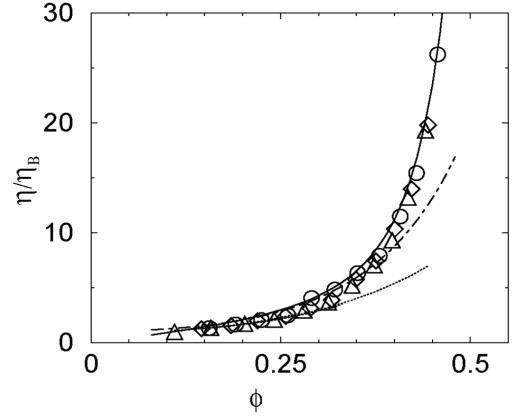

Fig. 3. Dependence of the scaled viscosity coefficient of argon on the packing index ϕ ($\circ$ – $T = 298$ K, $\diamond$ – $T = 1000$ K, and $\triangle$ – $T = 3000$ K) [3]

$$\eta_{\mathrm{B}} = 1.016 \frac{5}{16\sigma^2} \left(\frac{m k_{\mathrm{B}}T}{\pi}\right)^{1/2}. \tag{6}$$

The dimensionless combination $W_0/k_{\mathrm{B}}T$ used for the description of the dependence of the kinetic coefficients on the temperature and density is directly connected with the Carnahan–Starling equation [5]

$$\frac{W_0}{k_{\mathrm{B}}T} = \frac{p v_0}{k_{\mathrm{B}}T} = \frac{\phi \left(1 + \phi + \phi^2 - \phi^3\right)}{(1 - \phi)^3}, \tag{7}$$

where p stands for the pressure, $v_0 = \pi\sigma^3/6$ and $\phi = \frac{\pi\rho\sigma^3}{6}$ denotes the packing index, whereas σ is the effective diameter of an argon atom. The magnitude of the effective diameter can be obtained from the processing of data with the use of the Carnahan–Starling equation (7) with regard for Eq.(6). For example, at $T = 298$ K, $P = 1.3$ GPa, and the density of 1.95 g/cm^3, the value of the effective diameter $\sigma = 3.0965$ Å, at $T = 1000$ K, $P = 9.3$ GPa, and the density of 2.75 g/cm^3 – $\sigma = 2.7348$ Å. It is worth noting that these results are insufficient for the further analysis of the dependence of the self-diffusion coefficient on the density and temperature of a medium, because the pattern of intermolecular interaction essentially changes with increase in the density of the medium, which results in the dependence of the effective diameter on the density and temperature.

The numerical reproduction of $\sigma = \sigma(\rho, T)$ ca be obtained by means of the solution of the system of equations that approximate the experimental data
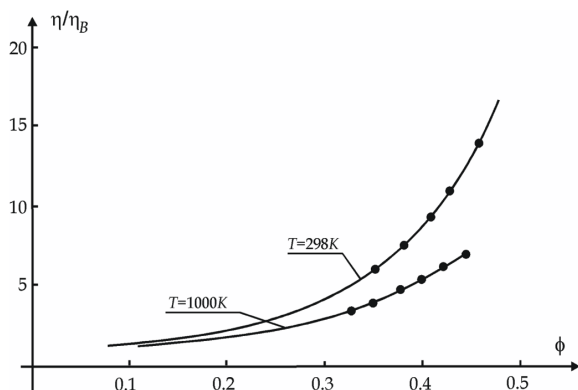
Fig. 4. Dependence of the scaled viscosity coefficient of argon [3, 4, 7] on the packing index ϕ. The circles denote the points used for the calculation of D_{col} by formula (2)

Fig. 5. Density dependence of the shear viscosity coefficient of argon

$D(\rho)$ [3]

$$\begin{cases} D^* = e^{-C_0 \frac{4\phi-3\phi^2}{(1-\phi)^2}}, \\ \frac{D}{D_{\mathrm{B}}} = e^{-\xi\varphi \frac{1+\phi+\phi^2-\phi^3}{(1-\phi)^3}}, \end{cases} \qquad (8)$$

where $D^* = \frac{D}{D_{\mathrm{B}}} \frac{2(1-\varphi)^3}{2-\varphi}$, $C_0 = 0.83$, and $\xi = 0.45$.

Using expressions (7) and (8), as well as the numerical values of the excess entropy calculated in [3],

$$\frac{s_e}{k_{\mathrm{B}}} = \phi \frac{4-3\phi}{(1-\phi)^2}, \qquad (9)$$

one can find the corresponding values of the density ρ and the effective diameter σ of particles (see the Table). However, the direct estimation of the relative value of the collective component of the self-diffusion coefficient D_{col}/D_s is related to one essential complication: the inadequate temperature dependence of the shear viscosity calculated in [3]. Using the values of η obtained in [3] as well as formula (4) for the scale factor η_{B}, it is easy to verify that, at fixed values of the density, the shear viscosity of the model system rises with increase in the temperature. From the physical viewpoint, this result is inadequate. It is worth noting that, at $\phi \leq 0.4$, one observes not only the incorrect
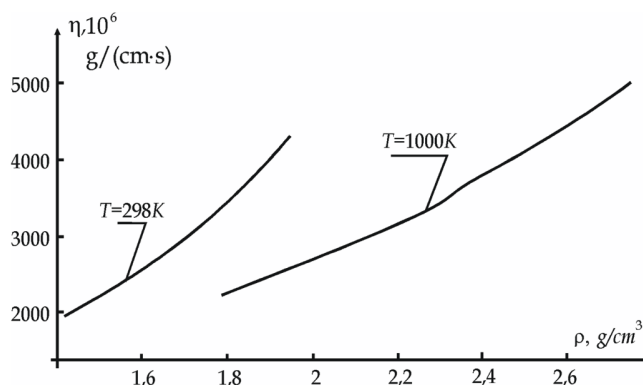
behavior of the dependences of the shear viscosity on the density and the temperature but also an essential deviation of the calculated values from those following from the Enskog theory [4,7] and having acceptable properties. At $\phi < 0.4$, the calculated values of η and those determined on the basis of the Enskog theory practically coincide.

Taking into account that the value $\phi = 0.4$ corresponds to $\rho \approx 1.8$ g/cm^3, i.e. to a rather high pressure, we accept that the temperature and density dependences of the viscosity of argon are described by the Enskog formulas [4,7,8] up to $\phi = 0.47$. The corresponding curves are presented in Figs. 4 and 5.

By using the extrapolated values of σ and η (see the Table), it is possible to estimate the collective component of the self-diffusion coefficient. The direct calculation by (2) shows that the relative value of the collective component of the self-diffusion coefficient systematically grows with increase in the density. At $\rho = 2.75$ g/cm^3 and the temperature $T = 1000$ K, it reaches 76%, $D_{\mathrm{col}} = 3.84 \times 10^{-5}$ cm^2/s. The quantity D_{col}/D_s also rises with increase in the temperature at a fixed density, which is naturally explained by the increase of the role of the vortex components of the fluctuation velocity field.

Values of the density, the corresponding effective diameter of molecules of liquid argon, and the diffusion and viscosity coefficients

$D \times 10^5$, cm^2/s	$\eta \times 10^6$, g/(cm·s)	ρ, g/cm^3	σ, Å	$D \times 10^5$, cm^2/s	$\eta \times 10^6$, g/(cm·s)	ρ, g/cm^3	σ, Å
–	–	–	–	24.36	2255	1.789	2.816
10.72	1967	1.42	3.151	16.51	2775	2.02	2.79
8.17	2363	1.54	3.145	12.72	3230	2.23	2.778
5.94	2895	1.69	3.124	9.25	3801	2.4	2.762
4.39	3494	1.807	3.107	6.88	4387	2.58	2.747
3.14	4313	1.95	3.096	5.07	5018	2.75	2.745
$P_{\max}=1.3$ GPa, $T=298$ K, $\sigma=3.0965$ Å				$P_{\max}=9.3$ GPa, $T=1000$ K, $\sigma=2.7346$ Å			

Thus, our initial prognosis about the growth of the role of the collective component of the self-diffusion coefficient with increase in the density of the system is qualitatively confirmed on the whole. We also plan to analyze the applicability of the Enskog approximation for the considered system in more details, as well as to perform a comparative analysis with a wider spectrum of experimental values of the self-diffusion and viscosity coefficients.

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ВПЛИВ ТИСКУ НА КОЛЕКТИВНИЙ ПЕРЕНОС
В ПРОСТИХ РІДИНАХ

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Р е з ю м е

На основі аналізу даних молекулярної динаміки самодифузії рідкого аргону з використанням рівняння стану Карнахана–Старлінга та моделі твердих сфер обчислено значення ефективного діаметра молекули. Показано, що внесок колективної складової коефіцієнта самодифузії у діапазоні високих тисків становить приблизно 76%.