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RESEARCH OF THE SHEAR AND VOLUME VISCOSITY COEFFICIENTS IN MULTIATOMIC LIQUIDS AND THEIR DEPENDENCES ON THE STATE PARAMETERS

The expressions for the shear, $\eta_S(\omega)$, and volume, $\eta_V(\omega)$, viscosity coefficients in multiatomic liquids have been obtained by solving the kinetic equations for one- and two-particle distribution functions, and their dependences on the thermodynamic state parameters have been analyzed. Numerical calculations of $\eta_S(\omega)$ and $\eta_V(\omega)$ are carried out for liquid N_2, O_2, CO, CO_2, and CH_4 in wide temperature, T, and density, ρ, intervals, at a fixed frequency ω, and for specific choices of the intermolecular interaction potential and the radial distribution function. The validity of the law of corresponding states for viscous properties of multiatomic liquids with respect to the reduced ρ^* and T^* values is tested. The results of theoretical calculations of the isofrequency viscosity coefficients for the examined liquids are found to be in satisfactory agreement with available experimental data.

Keywords: frequency dispersion, translational and structural relaxation, shear and volume viscosity coefficients, interaction potential, radial distribution function, liquid friction coefficient.

1. Introduction

Researches of the nonequilibrium properties of liquids and the restoration of an equilibrium structure in them are closely related to the study of the nature of internal relaxation processes and transfer phenomena. The latter are accompanied by dissipation phenomena, which are described with the use of the dynamic transport coefficients and the corresponding elastic moduli. Among the dynamic parameters of liquids, the dynamic shear, $\eta_S(\omega)$, and volume, $\eta_V(\omega)$, viscosity coefficient—as well as the dynamic moduli of shear, $\mu(\omega)$, and volume, $K(\omega)$, elasticity associated with the momentum flux transfer–are of special importance. The coefficient of shear viscosity was the best studied experimentally in wide density, ρ, pressure, P, temperature, T, and frequency, ω, intervals (see the detailed reviews [1–3]). However, it is impossible to determine the coefficient of volume viscosity and the dynamic moduli of shear and volume elasticity using direct experimental measurements. They can be found indirectly, by measuring other coefficients or physical parameters [4–7].

In work [7], the sound absorption coefficient was measured with a high accuracy for liquid Ar, Kr, and Xe in a vicinity of the corresponding ternary points. The results obtained do not correspond to the literature data for the volume viscosity η_V of simple liquids. The value of η_V does not vanish near the solidification point, and the ratio η_V/η_S gives underestimated values of about 0.3–0.5. This result differs from the theoretical value $\eta_V/\eta_S \approx 1.2$ obtained in the framework of the Enskog theory. However, it is in satisfactory agreement with the results calculated by applying the molecular dynamics method in the framework of the hard-sphere model.

It is known that, when considering the properties of a viscous compressible liquid, the account for both the shear and volume viscosity processes, which govern the energy losses under uniform compression and dilatation, is a compulsory rule. In work [8], a short review of the influence of the macroscopic dynamic shear viscosity η_S on a cylinder or a sphere rotating in a viscous liquid was given, and the formulas of the elementary theory of viscosity were also quoted. The concept of molecular viscosity was introduced. It was shown that, in the framework of a certain scenario, the coefficient of dynamic molecular shear viscosity and its temperature dependence can be obtained from the spectra of the scattering of depolarized light by molecules and from the dispersion law of electromagnetic waves in liquids consisting of molecules with a constant dipole moment. It was also emphasized that, for many organic liquids that absorb sound in the ultrasonic range, the coefficient η_V plays a more cricial role than η_S does.

In work [9], a review of physical methods applied to the measurement of viscosity coefficients in the most widespread class of anisotropic liquids, nematic liquid crystals, was made. The hydrodynamic Leslie–Ericksen–Parodi theory was expounded in brief, which demonstrates the availability of five independent viscosity coefficients. Anisotropic liquids have a feature in comparison with isotropic ones; this is the coefficient of rotational viscosity, which corresponds to the energy dissipation at liquid crystal reorientations. Estimations of the accuracy and the complexity of various measurement techniques were made.

The dispersion of the dynamic transport coefficients and the corresponding elastic moduli in simple liquids were numerically calculated in a wide interval of variation of thermodynamic state parameters and frequencies in works [10–12], using the molecular dynamics method. The frequency dispersion interval of those coefficients is wide. Probably, this fact stems from the low-frequency asymptotics of viscosity coefficients, $\sim\omega^{1/2}$, which are the Fourier transform of the autocorrelation functions at large times, which are proportional to $t^{-3/2}$.

Viscoelastic properties of classical liquids were studied in plenty of papers both on the basis of a phenomenological theory and the methods of statistical physics. The detailed reviews of those properties were made in works [1–3, 13, 14]. The method of kinetic theory [15, 15, 17, 18] was used to study the dynamic viscoelastic properties of simple one-atomic classical liquids–Ar, Kr, and Xe–and their dependences on the thermodynamic state parameters in a wide range of frequencies.

A lot of works were devoted to the experimental research of viscous properties of multiatomic liquids with quasi-spherical molecules. According to works [21–26], this class of liquids includes H_2, N_2, O_2, NO, NO_2, CO, CO_2, CH_4, CF_4, and others. Their viscoelastic properties were experimentally studied in wide intervals of variations of the density and the temperature. As was shown in work [24], the difference between the coefficients of volume and shear viscosity, as well as the distinction between the characteristic relaxation times of corresponding deformation types, can be explained using the same reasons as those for one-atomic liquids. It was also noticed that the vibrational relaxation does not affect experimental results, and the rotational degrees of freedom accelerate, to some extent, the momentum relaxation.

Liquids with molecules consisting of two or more atoms are known to possess, along with the translational degrees of freedom, the internal ones (rotational and vibrational). While studying the transfer phenomena in and the elastic properties of such liquids, it is necessary to consider the contributions made by rotational and vibrational relaxation processes. For this purpose, the initial kinetic equations describing the evolution of one-, $f_1(\mathbf{x}_1, t)$, and two-particle, $f_2(\mathbf{x}_1, \mathbf{x}_2, t)$, distribution functions must make allowance not only for the momentum, $\mathbf{p}$, and spatial-coordinate, $\mathbf{q}$, dependences, but also for the polar angles and the corresponding momenta, which is a complicated mathematical problem. Therefore, when analyzing the viscoelastic properties of liquids consisting of multiatomic molecules, we will confine the consideration to non-polar non-associating liquids composed of particles with the spherical, or close to it, symmetry, i.e. quasi-spherical molecules.

This work aimed at studying the dependences of shear, $\eta_S(\omega)$, and volume, $\eta_V(\omega)$, viscosity coefficients in multiatomic liquids on the thermodynamic state parameters, as well as carrying out the corresponding numerical calculations for liquid N_2, O_2, CO, CO_2, and CH_4 in a wide interval of variations of the density, ρ, and the temperature, T, at a fixed frequency ω.

2. Derivation of Analytical Expressions for the Viscosity Coefficients and the Choice of a Model

Let us use the microscopic definition of the stress tensor in classical liquids [17, 19] as a start point:

$$\sigma^{\alpha\beta}(\mathbf{q}_1,t)=\int\frac{\tilde{p}_1^{\alpha}\tilde{p}_1^{\beta}}{m}f_1(\mathbf{x}_1,t)d\mathbf{p}_1+$$
$$+\frac{\sigma^3}{2}\int\frac{\partial\Phi(|\mathbf{r}|)}{\partial r}\,\frac{r^{\alpha}r^{\beta}}{r}n_2(\mathbf{q}_1,\mathbf{r},t)d\mathbf{r},\qquad(1)$$

Here, $\mathbf{r}=(\mathbf{q}_2-\mathbf{q}_1)/\sigma$ is the reduced relative distance; σ is the diameter of a molecule, $\tilde{p}_1^{\alpha}=p_1^{\alpha}-m\vartheta^{\alpha}(\mathbf{q}_1,t)$ is the relative momentum; m, $\vartheta^{\alpha}(\mathbf{q}_1,t)$, and p_1^{α} are the mass and the components of the particle average velocity and momentum, respectively; $\mathbf{x}=\{\mathbf{q},\mathbf{p}\}$; $\mathbf{q}$ are the coordinates and $\mathbf{p}$ the momenta of the particles, $\Phi(|\mathbf{r}|)$ is the potential of intermolecular interaction, and

$$n_2\left(\mathbf{q}_1,\mathbf{q}_2,t\right)=\int f_2\left(\mathbf{x}_1,\mathbf{x}_2,t\right)d\mathbf{p}_1d\mathbf{p}_2\qquad(2)$$

is the nonequilibrium binary particle density in the configuration space; in essence, it is the momentum moment of the two-particle distribution function. In order to determine $\sigma^{\alpha\beta}(\mathbf{q}_1,t)$, let us use the following kinetic equations for the one-, $f_1(\mathbf{x}_1,t)$, and two-particle, $f_2(\mathbf{x}_1,\ \mathbf{x}_2,t)$, distribution functions obtained in work [19]:

$$\hat{L}_1f_1(\mathbf{x}_1,t)-\int\hat{\theta}_{12}f_2(\mathbf{x}_1,\mathbf{x}_2,t)d\mathbf{x}_2=$$
$$=\beta_1\frac{\partial}{\partial p_1^{\alpha}}\left[\frac{\tilde{p}_1^{\alpha}}{m}f_1(\mathbf{x}_1,t)+kT\left(\mathbf{q}_1,t\right)\,\frac{\partial f_1(\mathbf{x}_1,t)}{\partial p_1^{\alpha}}\right],\qquad(3)$$

$$(\hat{L}_{12}-\hat{\theta}_{12})f_2(\mathbf{x}_1,\mathbf{x}_2,t)-$$
$$-\int(\hat{\theta}_{13}+\hat{\theta}_{23})f_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,t)d\mathbf{x}_3=$$
$$=\sum_{i=1}^{2}\beta_i\frac{\partial}{\partial p_i^{\alpha}}\left[\frac{\tilde{p}_i^{\alpha}}{m}f_2(\mathbf{x}_1,\mathbf{x}_2,t)+\right.$$
$$\left.+\,kT(\mathbf{q}_i,t)\frac{\partial f_2(\mathbf{x}_1,\mathbf{x}_2,t)}{\partial p_i^{\alpha}}\right],\qquad(4)$$

where

$$\hat{L}_1=\frac{\partial}{\partial t}+\frac{p_1^{\alpha}}{m}\frac{\partial}{\partial q_1^{\alpha}};\quad \hat{L}_{12}=\frac{\partial}{\partial t}+\sum_{i=1}^{2}\frac{p_i^{\alpha}}{m}\frac{\partial}{\partial q_i^{\alpha}};$$

$$\hat{\theta}_{ij}=\frac{\partial\Phi(|\mathbf{q}_i-\mathbf{q}_j|)}{\partial q_i^{\alpha}}\frac{\partial}{\partial p_i^{\alpha}}+\frac{\partial\Phi(|\mathbf{q}_i-\mathbf{q}_j|)}{\partial q_j^{\alpha}}\frac{\partial}{\partial p_j^{\alpha}}$$

is the Chow–Uhlenbeck operator of interaction; β the coefficient of liquid friction; k the Boltzmann constant, and $T\left(\mathbf{q},t\right)$ the nonequilibrium temperature.

The system of equations (3) and (4) is not closed, but it is natural, because a complete isolation of a group of considered particles is impossible in a system with a great number of interacting particles. To close the system of those equations, we adopt the Kirkwood superposition approximation for $f_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,t)$:

$$f_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,t)=\frac{f_2(\mathbf{x}_1,\mathbf{x}_2,t)f_2(\mathbf{x}_1,\mathbf{x}_3,t)f_2(\mathbf{x}_2,\mathbf{x}_3,t)}{f_1(\mathbf{x}_1,t)f_1(\mathbf{x}_2,t)f_1(\mathbf{x}_3,t)}.\qquad(5)$$

Then, Eqs. (3)–(5) compose a closed system and allow the transfer phenomena and the elastic and acoustic properties of classical liquids to be studied.

Multiplying Eq. (3) by $\tilde{p}_1^{\alpha}\tilde{p}_1^{\beta}/m$ and integrating the product over the momenta $d\mathbf{p}_1$, we obtain a differential equation consisting of a sum of two terms, the kinetic part of the nonequilibrium pressure $p_k\left(\mathbf{q}_1,t\right)\delta^{\alpha\beta}$ and the kinetic part of the viscous stress tensor $k^{\alpha\beta}\left(\mathbf{q}_1,t\right)$. The equation for $k^{\alpha\beta}\left(\mathbf{q}_1,t\right)$ looks like

$$\frac{\partial k^{\alpha\beta}(\mathbf{q}_1,t)}{\partial t}+2n_0kT_0\left\{\frac{\partial\vartheta^{\alpha}\left(q_1,t\right)}{\partial q_1^{\beta}}\right\}=-\frac{1}{\tau}k^{\alpha\beta}(\mathbf{q}_1,t),\qquad(6)$$

where $\tau=m/2\beta$, m is the particle mass, β is the liquid friction coefficient, and

$$\left\{\frac{\partial\vartheta^{\alpha}}{\partial q^{\beta}}\right\}=\frac{1}{2}\left(\frac{\partial\vartheta^{\alpha}}{\partial q^{\beta}}+\frac{\partial\vartheta^{\beta}}{\partial q^{\alpha}}-\frac{2}{3}\delta^{\alpha\beta}\mathrm{div}\boldsymbol{\vartheta}\right).$$

On the other hand, the equation for the binary density in the configuration space, $n_2\left(\mathbf{q}_1,\mathbf{q}_2,t\right)$, can be obtained as follows. When integrating Eq. (4) over the momenta $d\mathbf{p}_1$ and $d\mathbf{p}_2$, and making allowance for expressions (2) and (5), we apply the method of momentum moment calculation for the two-particle distribution function $f_2\left(\mathbf{x}_1,\ \mathbf{x}_2,t\right)$. As a result, we obtain an equation for the binary density $n_2\left(\mathbf{q}_1,\mathbf{q}_2,t\right)$, which contains the divergences of higher moments. We take into account that the higher moments of the function $f_2\left(\mathbf{x}_1,\ \mathbf{x}_2,t\right)$ vary slowly in space and time. Then, changing from the coordinates $\mathbf{q}_1$ and $\mathbf{q}_2$ to the average, $\mathbf{q} = (\mathbf{q}_1 + \mathbf{q}_2)/2$, and relative, $\mathbf{r}_{12} = \mathbf{q}_2 - \mathbf{q}_1$, ones, expanding $n_2(\mathbf{q}_1, \mathbf{q}_2, t)$ and other functions entering those equations in Taylor series in a vicinity of the point $\mathbf{q}_1$, and assuming a weak spatial inhomogeneity of the liquid, we obtain, in a first approximation with respect to the parameter m/β, a heterogeneous equation of the parabolic type for the binary particle density in the configuration space, $n_2(\mathbf{q}_1, \mathbf{q}_2, t)$, i.e. the Smoluchowski equation, which looks like [17, 19]

$$\frac{\partial n_2(\mathbf{q}_1, \mathbf{r}, t)}{\partial t} + \omega_0 \hat{L} n_2(\mathbf{q}_1, \mathbf{r}, t) = F(\mathbf{q}_1, \mathbf{r}, t), \tag{7}$$

where

$$F(\mathbf{q}_1, \mathbf{r}_1, t) = -2n_2^0(|\mathbf{r}|)\left\{\left[1 + \frac{1}{6}\frac{\partial \ln g_0(r)}{\partial \ln r} - \right.\right.$$
$$\left.-\frac{1}{2}\left[n_0\left(\frac{\partial \ln g(r)}{\partial n_0}\right)_T + \gamma T_0\left(\frac{\partial \ln g(r)}{\partial T_0}\right)_n\right]\right] \times$$
$$\left.\times \operatorname{div} \boldsymbol{\vartheta} + \left(\frac{r^\alpha r^\beta - (1/3) r^2 \delta^{\alpha\beta}}{r^2}\right)\frac{\partial \ln g(r)}{\partial \ln r}\left\{\frac{\partial \vartheta^\alpha}{\partial q_1^\beta}\right\}\right\}, \tag{8}$$

$\hat{L} = -\frac{\partial}{\partial r^\alpha}\left[\frac{\partial}{\partial r^\alpha} - \frac{\partial}{\partial r^\alpha}\ln g_0(|\mathbf{r}|)\right]$ is the Smoluchowski operator in the configuration space; $\omega_0 = \tau_0^{-1} = 2kT/\beta\sigma^2$ is a phenomenological parameter, an analog of the diffusing molecule time; $n_2^0(|\mathbf{r}|) = n_0^2 g(r)$; $\gamma = (nc_v)^{-1}(\partial p/\partial T)_n$; n_0 and T_0 are the equilibrium density and temperature, respectively; and $g(r)$ is the equilibrium radial distribution function.

Equation (7) for $n_2(\mathbf{q}_1, \mathbf{r}, t)$ is a Cauchy problem $(t > 0, -\infty \le r \le \infty)$ with the initial condition

$$n_2(\mathbf{q}_1, \mathbf{r}, t) = \int_0^t dt_1 \int_{-\infty}^{\infty} G(r, r_1, t - t_1) F(\mathbf{q}_1, \mathbf{r}_1, t) d\mathbf{r}_1, \tag{9}$$

where

$$G(r, r_1, t - t_1) = \frac{2(r r_1)^{-1}}{(2\pi)^3}\left[\frac{\pi}{\omega_0(t - t_1)}\right]^{1/2} \times$$
$$\times\left\{\exp\left[-\frac{(r - r_1)^2}{4\omega_0(t - t_1)}\right] - \exp\left[-\frac{(r + r_1)^2}{4\omega_0(t - t_1)}\right]\right\}. \tag{10}$$

Expression (10) is a fundamental solution (Green's function) of Eq. ((7) for $n_2(\mathbf{q}_1, \mathbf{r}, t)$ and describes the temporal behavior of the binary density in the configuration space.

Making a Fourier transformation with respect to the time in Eqs. (1) and (6)–(9), we obtain the following expressions for the dynamic coefficients of shear and volume viscosity [16, 17]:

$$\eta_S(\omega) = \frac{nkT\tau}{1 + (\omega\tau)^2} + \frac{2\pi n^2 \sigma^3}{15} \times$$
$$\times \int_0^\infty dr\, r^3 \frac{\partial \Phi(|\mathbf{r}|)}{\partial r} \int_{-\infty}^{\infty} G_1(r, r_1, \omega) \frac{\partial g(|\mathbf{r}_1|)}{\partial r_1} r_1 d\mathbf{r}_1, \tag{11}$$

$$\eta_V(\omega) = \frac{2\pi n^2 \sigma^3}{3} \times$$
$$\times \int_0^\infty dr\, r^3 \frac{\partial \Phi(|\mathbf{r}|)}{\partial r} \int_{-\infty}^{\infty} G_1(r, r_1, \omega)\, \varphi_0(|\mathbf{r}|_1) d\mathbf{r}, \tag{12}$$

where

$$G_1(r, r_1, \omega) = \frac{\tau_0 (2\omega\tau_0)^{-1/2}}{4\pi r r_1} \times$$
$$\times\left[e^{-\varphi_1}(\sin\varphi_1 - \cos\varphi_1) - e^{-\varphi_2}(\sin\varphi_2 - \cos\varphi_2)\right]; \tag{13}$$

$$\varphi_0(|\mathbf{r}_1|) = \frac{r_1}{3}\frac{\partial g(r_1)}{\partial r_1} - \left[n\left(\frac{\partial g(r_1)}{\partial n}\right)_T + \gamma T\left(\frac{\partial g(r_1)}{\partial T}\right)_n\right];$$

$$\varphi_{1,2} = \varphi_{1,2}(r, r_1, \omega) = \left(\frac{\alpha\tau_0}{2}\right)^{-1/2}(r \mp r_1),$$

$$\varphi_{1,2} = \varphi_{1,2}(r, r_1, \omega) = \left(\frac{\alpha\tau_0}{2}\right)^{-1/2}(r \mp r_1),$$

$\alpha = (2\omega\tau_1)^{1/2}$, and $\omega = 2\pi\nu$ is the cyclic frequency of the process. Formulas (11)–(13) describe the dynamic behavior of the viscosity coefficients $\eta_S(\omega)$ and $\eta_V(\omega)$ of the liquid in a wide range of the frequency. The first term in Eq. (11) makes allowance for the contribution of the stress tensor relaxation in the momentum space, i.e. the translational relaxation, the characteristic time of which equals $\tau = m/2\beta$. However, the frequency dependences of $\eta_S(\omega)$ and $\eta_V(\omega)$ are mainly described by the Fourier transform of the spatial and temporal behaviors of the fundamental solution (Green's function) of the Smoluchowski equation for the binary density $n_2(\mathbf{q}_1, \mathbf{r}, t)$ in the configuration space. This solution, $G_1(r, r_1, \omega)$, has a low-frequency asymptotics coinciding with the results obtained in the framework of the molecular dynamics method [10–12].

In order to determine the coefficients $\eta_S(\omega)$ and $\eta_V(\omega)$, and to carry out numerical calculations according to expressions (11)–(13), we also need such molecular parameters of the liquid as the mass m and the diameter d of a particle, the potential well depth ε, the relaxation times τ and τ_0, and the liquid friction coefficient β. They were determined and studied in works [16, 17]. In particular,

$$\beta^2 = (4\pi/3)\rho\,\sigma \int_0^\infty \nabla^2\,\Phi(|\mathbf{r}|)\,g(|\mathbf{r}|)r^2\,dr, \tag{14}$$

where ρ is the liquid density, $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$ is the radial part of the Laplace operator, $\Phi(|\mathbf{r}|)$ the Lennard-Jones potential, and r the dimensionless relative distance.

Hence, while studying the nature of the coefficients β, $\eta_S(\omega)$, and $\eta_V(\omega)$ and determining their dependences on the state parameters, one must select the potential $\Phi(|\mathbf{r}|)$ and the radial distribution function $g(|\mathbf{r}|)$. In our research dealing with the viscous properties of liquids consisting of multiatomic molecules, we confine the consideration to non-polar non-associating liquids composed of particles with the spherical symmetry or the symmetry close to it, i.e. we assume the molecules to be quasi-spherical. For the latter, the most optimum initial model is a model with the modified Lennard-Jones potential $\Phi(|\mathbf{r}|)$ considered in works [16, 17],

$$\Phi(|\mathbf{r}|) = \begin{cases} \infty, & \text{for } r < 1, \\ 4\varepsilon\left(r^{-12} - 0,5r^{-6}\right), & \text{for } r \geq 1. \end{cases} \tag{15}$$

Following work [20], the radial distribution function is written down as follows:

$$g_0(r,\rho,T) = y(r,\rho^*)\,e^{-\frac{\Phi(|\mathbf{r}|)}{kT}}, \tag{16}$$

where $y(r,\rho^*)$ is the binary distribution function for two cavities.

It should be noted that, for the function $y(r,\rho^*)$, there exists an analytical solution of the Percus–Yevick equation for hard spheres at a distance $1 < r < 5$ [20, 21]. However, since the analytical expressions for β, $\eta_S(\omega)$, and $\eta_V(\omega)$ are involved, we confine the analysis, in the first approximation, to the contact value $y(r,\rho^*) = y(\rho^*)$ at the distance $r = 1$ $(r = d)$ obtained by N.F. Carnahan and K.E. Starling in the form

$$y(\rho^*) = (2-\rho^*)/2(1-\rho^*)^3, \tag{17}$$

where $\rho^* = \frac{\pi}{6}nd_3 = \frac{\pi}{6}\rho\frac{d_3N_0}{M}$ is the reduced density, ρ the solution density, N the Avogadro number, and M the molar mass.

Hence, the obtained analytical expressions (11)–(17) allow us to carry out numerical calculations for the isofrequency coefficients of shear and volume viscosity in multiatomic liquids with quasi-spherical molecules, as well as for their dependences on the thermodynamic state parameters.

3. Results of Numerical Calculations

On the basis of formulas (11) and (12) with regard for expressions (13)–(17), we numerically calculated the coefficients of shear, η_S, and volume, η_V, viscosity and their ratio η_S/η_V for liquid N_2, O_2, CO, CO_2, and CH_4 at the fixed frequency $\nu^* = 10^{-6}$ ($\nu = 10^7$ Hz) and compared them with experimental data [22, 23, 25, 27]. The calculations were carried out for the following temperature intervals and the corresponding densities of liquids: 80 K $\leq T \leq$ 120 K for N_2, 80 K $\leq T \leq$ 146 K for O_2, 71.48 K $\leq T \leq$ 76.34 K for CO, 224.3 K $\leq T \leq$ 303.2 K for CO_2, and 91.01 K $\leq T \leq$ 114.13 K for CH_4. In Tables 1 and 2 and in Figs. 1 and 2, the obtained results for the coefficients η_S and η_V in those liquids are compared with experimental data. It should be noted that, in the tables, we show the available experimental results for η_S and η_V. In the case where the experimental data for η_V were absent, we give the relevant values calculated by us theoretically.

The theoretical and experimental data in Tables 1 and 2 for the temperature and density dependences of η_S are in satisfactory quantitative agreement. For η_V, the experimental and theoretical values are also in quantitative agreement; however, the temperature dependences are different. Namely, as the temperature increases, the experimental values of η_V grow, whereas the theoretically calculated ones, as well as other transfer coefficients, monotonously fall down. The origin of this discrepancy may probably consist in the following. It is known that the coefficient of volume viscosity η_V for liquids cannot be determined using direct experimental measurements. It can be found by analyzing the excess absorption of sound waves in liquids. According to work [6], the determination accuracy of η_V in liquids, owing to the measurement errors for the Stokes sound absorption coef-

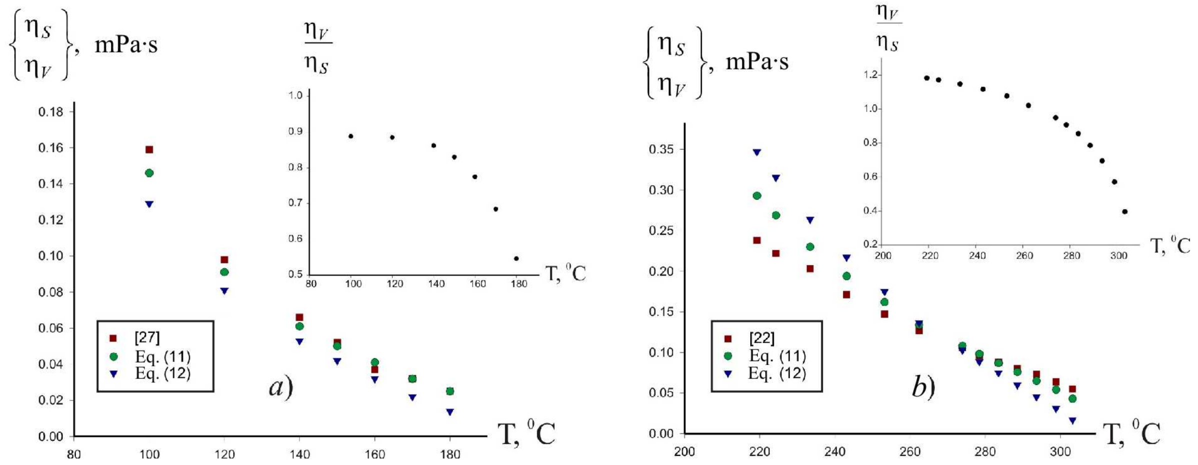

Fig. 1. Dependences of the coefficients η_S and η_V on the temperature at $\nu^* \sim 10^{-6}$ ($\nu \sim 10^7$ Hz) for (a) methane and (b) carbon dioxide

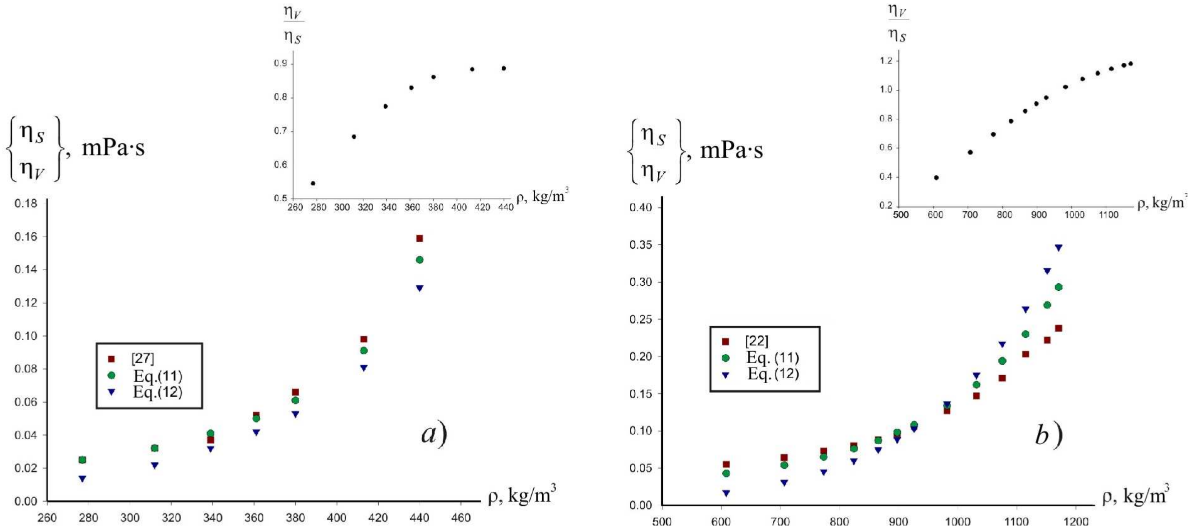

Fig. 2. Dependences of the coefficients η_S and η_V on the density at $\nu^* \sim 10^{-6}$ ($\nu \sim 10^7$ Hz) for (a) methane and (b) carbon dioxide

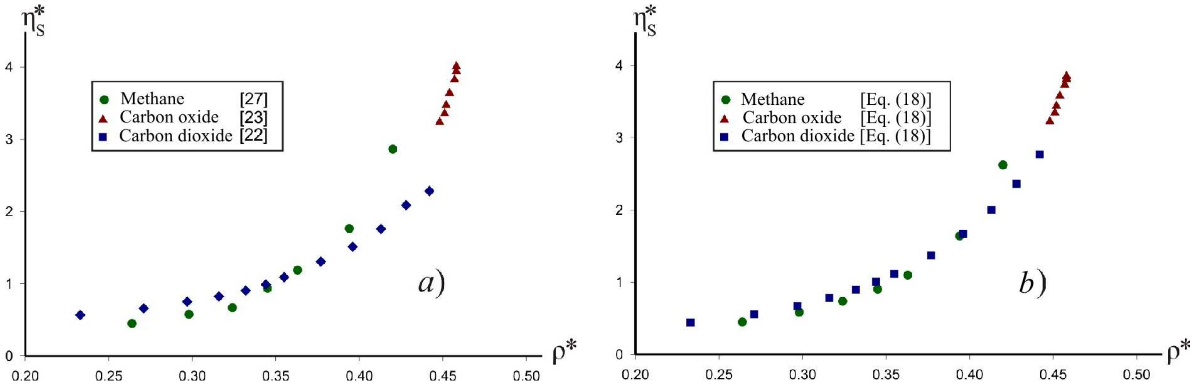

Fig. 3. Dependences of the reduced shear viscosity on the reduced density: (a) experimental and (b) theoretical results

Table 1. **Viscosity coefficients η_S and η_V for liquid nitrogen and oxygen at $\nu^* \sim 10^{-6}$**

T, K [25]	ρ, kg/m^3 [25]	η_S, mPa·s		η_V, mPa·s		η_V/η_S	
		[25]	formula (11)	[25]	formula (12)	[25]	formula (12)/(11)
				Nitrogen			
80	774	0.140	0.124	0.097	0.112	0.693	0.903
90	744	0.101	0.087	0.086	0.077	0.851	0.885
100	688	0.075	0.062	0.090	0.052	1.200	0.839
110	623	0.056	0.045	0.099	0.034	1.768	0.756
115	581	0.045	0.037	0.140	0.025	3.111	0.676
120	527	0.037	0.029	0.203	0.017	5.486	0.586
				Oxygen			
80	1190	0.256	0.261	0.110	0.238	0.430	0.912
90	1142	0.197	0.185	0.103	0.167	0.523	0.903
100	1090	0.154	0.138	0.111	0.124	0.721	0.899
110	1035	0.123	0.107	0.116	0.094	0.943	0.879
120	974	0.101	0.084	0.121	0.071	1.198	0.845
130	903	0.079	0.065	0.130	0.051	1.646	0.785
140	813	0.062	0.048	0.167	0.032	2.694	0.667
146	741	0.050	0.039	0.267	0.022	5.340	0.564

Table 2. **Viscosity coefficients η_S and η_V for liquid methane at $\nu^* \sim 10^{-6}$**

Methane									
T, K [23]	ρ, kg/m^3 [23]	η_S, mPa·s		T, K [27]	ρ, kg/m^3 [27]	η_S, mPa·s		η_V, mPa·s	η_V/η_s
		[23]	formula (11)			[27]	formula (11)	formula (12)	formula (11)/(12)
91,01	453	0.199	0.195	100	440	0.159	0.146	0.129	0.888
93.77	450	0.182	0.179	120	413	0.098	0.091	0.081	0.885
97.34	446	0.162	0.162	140	380	0.066	0.061	0.053	0.862
100.88	441	0.146	0.147	150	361	0.052	0.05	0.042	0.83
103.84	437	0.138	0.135	160	339	0.037	0.041	0.032	0.775
107.05	433	0.127	0.124	170	312	0.032	0.032	0.022	0.685
109.76	429	0.12	0.116	180	277	0.025	0.025	0.014	0.546
114.13	422	0.112	0.104						

ficient α and the errors in the data on thermodynamic and transport properties of liquids (the density ρ; the sound velocity c; the isobaric, C_P, and isochoric, C_V, heat capacities; the shear viscosity η_S, and the thermal conductivity λ), is insufficient for obtaining the accurate experimental dependences and making their comparison with the theory.

For the most illustrative representation of the results obtained in theoretical calculations and their comparison with experimental data, the temperature dependences of η_S, η_V, and their ratio η_V/η_S are depicted for liquid CH_4 and CO_2 in Fig. 1 (panels *a* and *b*, respectively); the corresponding density dependences are depicted in Fig. 2. One can see that all calculated dependences for the liquids concerned

Table 3. **Viscosity coefficients η_S and η_V for liquid carbon oxide and carbon dioxide at $\nu^* \sim 10^{-6}$**

Carbon oxide						Carbon dioxide					
T, K [23]	ρ, kg/m^3 [23]	η_S, mPa·s		η_V, mPa·s	η_V/η_S	T, K [22]	ρ, kg/m^3 [22]	η_S, mPa·s		η_V, mPa·s	η_V/η_S
		[23]	formula (11)	formula (12)	formula (12)/(11)			[22]	formula (11)	formula (12)	formula (12)/(11)
71.48	836	0.239	0.23	0.239	1.042	224.3	1151.5	0.222	0.269	0.315	1.172
71.78	835	0.235	0.227	0.237	1.042	233.4	1115.1	0.203	0.230	0.264	1.148
72.30	833	0.228	0.223	0.232	1.041	243.1	1075.4	0.171	0.194	0.217	1.117
73.45	829	0.217	0.214	0.222	1.041	253.2	1031.6	0.147	0.162	0.175	1.077
74.60	825	0.207	0.205	0.213	1.040	262.4	982.2	0.127	0.134	0.136	1.022
75.34	822	0.200	0.200	0.207	1.040	273.9	926.4	0.106	0.108	0.103	0.949
76.34	818	0.193	0.192	0.200	1.039	278.4	897.8	0.096	0.098	0.089	0.907
						283.5	865.6	0.088	0.087	0.075	0.856
						288.5	824.4	0.08	0.076	0.060	0.786
						293.6	773.5	0.073	0.065	0.045	0.695
						298.8	706.7	0.064	0.054	0.031	0.571
						303.2	608.6	0.055	0.043	0.017	0.396

Table 4. **Experimental and theoretical values of η_S^* in liquids for various reduced ρ^* and T^***

Methane				Carbon oxide				Carbon dioxid			
T^*	ρ^*	η_s^*		T^*	ρ^*	η_s^*		T^*	ρ^*	η_s^*	
		[27]	formula (18)			[23]	formula (18)			[22]	formula (18)
0.673	0.420	2.864	2.624	0.726	0.458	4.010	3.855	1.187	0.442	2.284	2.769
0.808	0.394	1.765	1.640	0.729	0.458	3.943	3.813	1.235	0.428	2.088	2.365
0.942	0.363	1.189	1.098	0.735	0.457	3.826	3.736	1.286	0.413	1.759	2.000
1.010	0.345	0.937	0.904	0.746	0.454	3.641	3.584	1.340	0.396	1.512	1.671
1.077	0.324	0.667	0.736	0.758	0.452	3.473	3.443	1.388	0.377	1.306	1.373
1.144	0.298	0.576	0.585	0.766	0.451	3.356	3.348	1.449	0.355	1.090	1.114
1.212	0.264	0.450	0.450	0.776	0.448	3.238	3.227	1.473	0.344	0.988	1.005
								1.500	0.332	0.905	0.899
								1.526	0.316	0.823	0.785
								1.553	0.297	0.751	0.671
								1.581	0.271	0.658	0.558
								1.604	0.233	0.566	0.442

are in satisfactory quantitative agreement with experimental data. This fact may result from a correct account of the dependences of the friction coefficient β and the relaxation times τ and τ_0 on the thermodynamic state parameters for those multiatomic liquids.

On the basis of the analytical expressions obtained for η_S and η_V, let us examine the validity of the law of corresponding states for the viscoelastic properties of multiatomic liquids with quasi-spherical molecules in relation with the thermodynamic state parameters ρ and T. The reduced coefficients of shear, η_S^*, and volume, η_V^*, viscosity look like

$$\eta_S^* = \frac{\sigma^2}{\sqrt{m\varepsilon}}\,\eta_S(\omega); \quad \eta_V^* = \frac{\sigma^2}{\sqrt{m\varepsilon}}\,\eta_V(\omega). \tag{18}$$

The results of corresponding numerical calculations are quoted in Table 4 and shown in Fig. 3. One can see that, for the viscous properties of multiatomic liquids with quasi-spherical molecules, the validity of the law of corresponding state depends on the thermodynamic state parameters ρ and T.

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ДОСЛІДЖЕННЯ КОЕФІЦІЄНТІВ ЗСУВНОЇ І ОБ'ЄМНОЇ В'ЯЗКОСТІ БАГАТОАТОМНИХ РІДИН ЗАЛЕЖНО ВІД ПАРАМЕТРІВ СТАНУ

Резюме

Досліджено залежність коефіцієнтів зсувної $\eta_S\,(\Omega)$ і об'ємної $\eta_V\,(\omega)$ в'язкості багатоатомних рідин, отриманих на основі кінетичних рівнянь для одночасткової $f_1(\mathbf{x}_1, t)$ і двочастинкової $f_2(\mathbf{x}_1, \mathbf{x}_2, t)$ функцій розподілу, від термодинамічних параметрів стану. Проведено чисельні розрахунки коефіцієнтів $\eta_S(\omega)$ і $\eta_V(\omega)$ для рідких N_2, O_2, CO, CO_2, CH_4 при певному виборі потенціалу міжмолекулярної взаємодії $\Phi(|\mathbf{r}|)$ і радіальної функції розподілу $g\,(|\mathbf{r}|)$ у широкому інтервалі зміни температури T і щільності ρ при фіксованій частоті ω. Досліджено виконання закону відповідних станів для в'язких властивостей багатоатомних рідин в залежності від наведених ρ^* і T^*. Отримані результати теоретичних розрахунків ізочастотних коефіцієнтів в'язкості цих рідин знаходяться в задовільній згоді з наявними в літературі експериментальними даними.