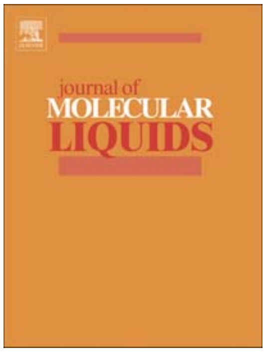

Nature of the kinematic shear viscosity of low-molecular liquids with averaged potential of Lennard-Jones type

Pavlo V. Makhlaichuk, Victor N. Makhlaichuk, Nikolay P. Malomuzh

PII: S0167-7322(15)30364-0
DOI: doi: 10.1016/j.molliq.2016.11.101
Reference: MOLLIQ 6648

To appear in: *Journal of Molecular Liquids*

Received date: 18 August 2015
Revised date: 21 October 2016
Accepted date: 25 November 2016

Please cite this article as: Pavlo V. Makhlaichuk, Victor N. Makhlaichuk, Nikolay P. Malomuzh, Nature of the kinematic shear viscosity of low-molecular liquids with averaged potential of Lennard-Jones type, *Journal of Molecular Liquids* (2016), doi: 10.1016/j.molliq.2016.11.101

Nature of the kinematic shear viscosity of low-molecular liquids with averaged potential of Lennard-Jones type

Pavlo V. Makhlaichuk, Victor N. Makhlaichuk[*]*, Nikolay P. Malomuzh*

Dept. of Theoretical Physics, Odessa National University, 2 Dvoryanskaja str., Odessa, 65082, Ukraine

---

[*] Corresponding author.

E-mail addresses:mahlaichuk@gmail.com(P.V. Makhlaichuk),interaktiv@ukr.net(V. N. Makhlaichuk),malomuzhnp@list.ru(N.P. Malomuzh).

Abstract

The main attention is focused on the kinematic shear viscosity of argon, nitrogen, benzene and nitrobenzene which have different molecular shapes and sizes and intermolecular interactions, as well. We show that all these liquids demonstrate the argon-like behavior of their kinematic shear viscosities and belong to the same similarity class. Additionally, we show that the kinematic shear viscosity of argon is mainly determined by the packing factor which is characteristic for the van der Waals equation of state. We suggest the explicit formula for the shear viscosity. We found out that the similarity in the behavior of the shear viscosities of low-molecular liquids is connected with the identical structure of their averaged interparticle potentials for enumerated and other low-molecular liquids. This circumstance is a consequence of rotational motion of molecules in liquids.

I. Introduction

The temperature dependence of the shear viscosity of low molecular liquids, as a rule, is described by the sum of exponents [1-3]:

$$\eta = \eta_1 \exp(\varepsilon_1 / t) + \eta_2 \exp(\varepsilon_2 / t) + \dots , \qquad (1)$$

where $t = T / T_c$ is the dimensionless temperature and T_c is the critical temperature of the water (the Boltzmann constant is put to be unity). Such form for the shear viscosity reflects the applicability of crystal-like representations for the description of thermal motion in them [4]. In this case, molecules of liquids oscillate near their temporary equilibrium positions during the typical time τ_0 and after this they displace to the other temporary equilibrium positions. If the typical time τ_1 of this displacement is considerably smaller than τ_0, one can speak about the applicability of crystal-like representations. The application of the activation theory [4-5] is the natural way to describe transport processes in such systems.

Explicitly, this approach is not applicable for argon, where molecules chaotically drift inside the system. The formal application of the exponential approximation (1) for the shear viscosity of argon is conjugated with a serious contradiction: the activation energy is proved to be less than the thermal motion energy ($\varepsilon_{Ar} < t$) [6]. This circumstance is very important, though, it is often ignored. Liquid argon is one of the simplest dense systems, however, the satisfactory methods to the describe its shear viscosity are absent. All results obtained for gases [7] do not work since methods of kinetic theory are not applicable. Modifications of kinetic approaches of type [8-9] are not satisfactory, either. Therefore, phenomenological attempts are frequently used to construct the shear viscosity. Here we mention only one of the old works [10] as well as the attempt undertaken in [11]. Unfortunately, the special consideration of the shear viscosity of argon within these approaches was not carried out.

The main goal of this paper is the analysis of physical nature of kinematic shear viscosity for liquid argon, nitrogen, benzene and nitrobenzene as well as for other liquids with similar intermolecular interactions. The choice of the objects to investigate is motivated by the following: argon molecules have the spherical shape and their interaction is described by the simplest interparticle potential which is usually modeled by the Lennard-Jones one [12]; a molecule of nitrogen has a linear dumbbell-like shape, it has not only a translational motion but it also rotates; the intermolecular potential is a combination of dispersive forces of argon-like type and electrostatic quadrupole interactions [13]. However, due to the rotation of molecules, the angular dependence of their interparticle potentials becomes considerably irrelevant. Moreover, the total field acting on a molecule from the side of weakly ordered neighbours is quasi-spherical, i.e. the angular correlations play inessential role. The same situation is characteristic for benzene, which molecules have a ring-like shape. Here the interparticle potential is similar to that for nitrogen molecules. The replacement of hydrogen by a NO_2-group modifies the shape of a nitrobenzene molecule and leads to the appearance of dipole moment and rather strong dipole-dipole interactions between two molecules. However, the superposition effects of dipole fields, created by surrounding molecules, result in a considerable attenuation of the acting field that is why the selected molecule rotates quasi-freely.

Thus, comparing the behaviour of the kinematic shear viscosities for all enumerated liquids we can understand the role of molecular shape and intermolecular interactions of different types.

II. Guiding principles

We will follow the general principles: the kinematic shear viscosity of dense gas and liquid of anisotropic molecules is mainly determined by the parameters of the averaged intermolecular potential; the last has a similar form, close to the Lennard-Jones potential for different liquids. As a result, we expect that their equations of state and the kinematic shear viscosity will satisfy the similarity principle for corresponding states. It is appropriate to note that the last also helps to describe the nontrivial peculiarities of relaxation processes in highly viscous liquids [14].

In accordance with the similarity principle for corresponding states we are going to discuss the relation between normalized quantities. So, we will use the normalized kinematic shear viscosity $\tilde{\nu} = \nu / \nu_R$, where ν_R is the regularized value of the shear viscosity. The last is defined as $\nu_R = \nu(T_R)$, where T_R is the temperature of regularization. The normalized temperature is: $t = T / T_R$. The regularized value of the specific volume is defined : $\tilde{\upsilon} = \upsilon / \upsilon_R$, where $\upsilon_R = \upsilon(t = 1)$, or $\upsilon_R = \upsilon(T_R)$. In both cases values of the kinematic shear viscosity and specific volume are taken on the coexistence curve where they depend only on temperature. It is worth noting that the regularization temperature t_R divides the thermodynamic and fluctuation regions, i.e. it takes the same meaning as the Ginzburg temperature [15] does. The numerical value of T_R is very close to T_c (see in the Table 1, where $t_R = T_R / T_c$). The value of ν_R is practically coincides with that obtained with the help of parabolic extrapolation from the range adjacent to the fluctuation region [15]. Let us introduce also the parameter λ ($\lambda < 1$) as the proportionality coefficient between υ_R and the specific volume at the critical point: $\upsilon_R = \lambda \cdot \upsilon_c$. Due to λ we can exclude the influence of dimers, trimers and clusters of higher order arising near the critical point [16, 17] and essentially changing properties of systems.

The fact that the averaged intermolecular potentials of nitrogen, benzene and nitrobenzene are similar to the Lennard-Jones potential is quite natural. Indeed, the deviation of intermolecular potential from the argon-like one is caused by electrostatic interactions. Their long-range asymptotes are approximated by the multipole expansion, among which the leading role belongs to the dipole-dipole interaction. It can be verified that the averaged dipole-dipole potential decays similarly to that of the potential of dispersive forces. The numerical analysis (see below) shows that the deviation from argon-like potential on short distances is also inessential.

In general, the interparticle potential in liquid gets the following form:

$$\Phi(q_1,q_2)=\Phi_0(q_1,q_2)+\Phi_w(q_1,q_2)+\Phi_e(q_1,q_2)+\Phi_H(q_1,q_2)\,, \qquad (2)$$

where q_i, $i=1,2$, is the full set of the translational and angular coordinates of $i-th$ molecule. The first and the second terms in (2) describe the hard-core repulsion and the dispersive (van der Waals) attraction between molecules, $\Phi_e(q_1,q_2)$ - the electrostatic multipole interaction and $\Phi_H(q_1,q_2)$ is the irreducible contribution, related to H-bonds. The last ones are formed, in particular, between water and alcohol molecules, however, their contributions, in comparison with the electrostatic ones, are small [18-20].

We use the perturbation theory to describe the thermodynamic properties of liquids [21]. The zero approximation corresponds to hard-core contribution in (2). All other terms in (2) are considered as perturbations. Here, we will suppose that the behaviour of the kinematic shear viscosity in liquids, especially near their triple points, is also mainly determined by hard-core effects. In other words, we expect that the behavior of the shear viscosity in suitable variables is to be argon-like.

III. Qualitative reasons for the character of the argon kinematic shear viscosity

The kinematic shear viscosity of liquid argon, as it was shown in [22, 23], is described by the formula

$$\tilde{\nu}(\upsilon,t)=\frac{\zeta_0}{(\tilde{\upsilon}-\tilde{\upsilon}_0(t))^{1/3}}\,, \qquad (3)$$

where $\upsilon_0(t)$ is the excluded volume and the parameter ζ_0 is practically constant, close to unity.

Now let us discuss the physical nature of the formula (3). It cannot be a result of some kinetic theory since the quite satisfactory kinetic equation for liquids is absent. In this case it is necessary to apply a more adequate model for the formation of the kinematic shear viscosity in liquids.

First of all, the packing factor χ is to be taken into account, similarly to that of the van der Waals equation of state.

Indeed, the shear viscosity in liquids arises due to friction effects between the two nearest layers. These effects are caused by quasi-mechanical friction between rough surfaces.The transport of impulse by molecules transferring from one layer to another is small because a molecule surrounded by its nearest neighbours is similar to particle locked in a cage. The value of friction is proportional to the number of contacting molecules, i.e. $\sim n_{cont}^{2} \sim 1/\upsilon^{2/3}$, as well as it is inverse proportional to distance between the two nearest layers: $\sim 1/(\upsilon - \upsilon_0)^{1/3}$, moving relatively to each other. In other words, the friction is proportional to the packing factor: $\chi = \chi(1/(\upsilon - \upsilon_0)^{1/3})$. Except very high pressures and deforming molecules, we can take no more then the one term of expansion: $\chi \sim 1/(\upsilon - \upsilon_0)^{1/3}$. The formula (3) is the intermediate consequence such approach.

It is necessary to stress that the weak interchange of molecules between the nearest layers is naturally explained by small value of free volume in all liquids.The molecular transport of impulse becomes noticeable when approaches the critical point, where the density essentially decreases.

The analogous reasons are expected to be correct for liquids with nonspherical molecules, in particular for liquid nitrogen, benzene and nitrobenzene.

Note, that (3) reminds us the well known Bachinskii’s formula [24]:

$$\tilde{\nu}_B(\tilde{\upsilon}, t) \approx \frac{\zeta_B}{\upsilon - \upsilon_0}.$$

It quite satisfactory fits experimental data [24] only for narrow intervals of variations of υ. Another important circumstance is illustrated in Fig.1 where the temperature dependences of the combination

$$\zeta_0(p,t) = \tilde{\nu}^{1/p}(t)(\tilde{\upsilon}(t) - \tilde{\upsilon}_0) \tag{4}$$

of different p and constant $\tilde{\upsilon}_0$ are represented. Here the values of $\tilde{\upsilon}_0$ and ζ_0 are also some functions of p.

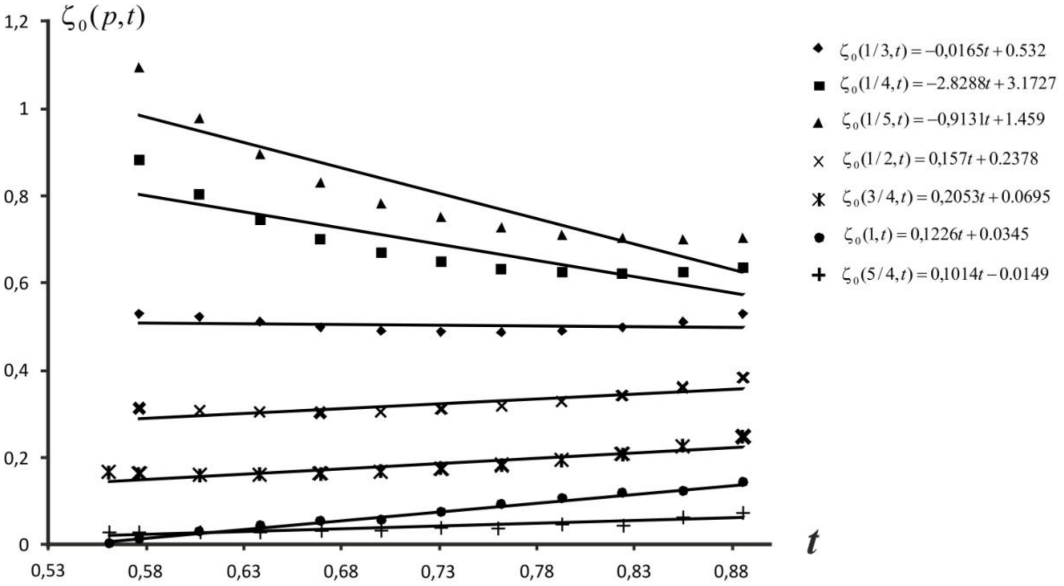

Fig.1. Temperature dependences of $\zeta_0(p,t)$ for argon obtained with the help (11) and $p = 0.2, 0.25, 1/3, 0.5, 0.75, 1, 1.25$: straight lines are fitted to experimental data by means of the least-square method.

The optimal value of $p = 1/3$ also appears straight after the attempt to fit experimental values of $\ln \tilde{\nu}(\tilde{\upsilon}, t)$ with the help of linear polynomial: $p \ln(\tilde{\upsilon} - \tilde{\upsilon}_0) + \ln \zeta_0$, where $\tilde{\upsilon}_0$ is expected to be equal to $\tilde{\upsilon}_{tr} = \upsilon_{tr} / \upsilon_R$, and υ_{tr} is the specific volume at the triple point [22].

It is appropriate to note that the values of ζ_0 and $\tilde{\upsilon}_0$ are not independent. Indeed, the kinematic shear viscosity near the critical point satisfies the limit equation:

$$\lim_{t\to 1}\tilde{\nu}(\tilde{\upsilon},t)=1, \tag{5}$$

so $\zeta_0=(1-\tilde{\upsilon}_0)^{1/3}$. Thus, we get that the kinematic shear viscosity of argon is described by the expression:

$$\tilde{\nu}(\tilde{\upsilon},t)\approx\frac{(1-\tilde{\upsilon}_0)^{1/3}}{(\tilde{\upsilon}-\tilde{\upsilon}_0)^{1/3}}. \tag{6}$$

The consistency of (5) and (6) is guaranteed if

$$\nu_R=\nu(\upsilon(t_R),t_R)\approx\nu(\upsilon_R). \tag{7}$$

Since $\upsilon_R=\upsilon(t_R)$, the definition $\upsilon_R=\lambda\upsilon_c$ leads to the equation: $\upsilon(t_R)=\lambda\upsilon_c$ for the determination of t_R. Thus, λ remains to be practically one nontrivial adjustable parameter (although approximate value of $\lambda\approx 0.8$ is known a priori since t_R has the same meaning as the Ginzburg temperature $t_G=T_G/T_c$ [15]. Vice versa, t_R can be used as the independent estimate for t_G).

The main prediction following from (3) and (6) is the constancy of the kinematic shear viscosity for all liquid states on isochors. This fact is supported with high accuracy by experimental data presented in Fig.2. The small deviations from constants are naturally taken into account with the help of the weak temperature dependence of the excluded volume: $\tilde{\upsilon}_0$ (see Discussion).

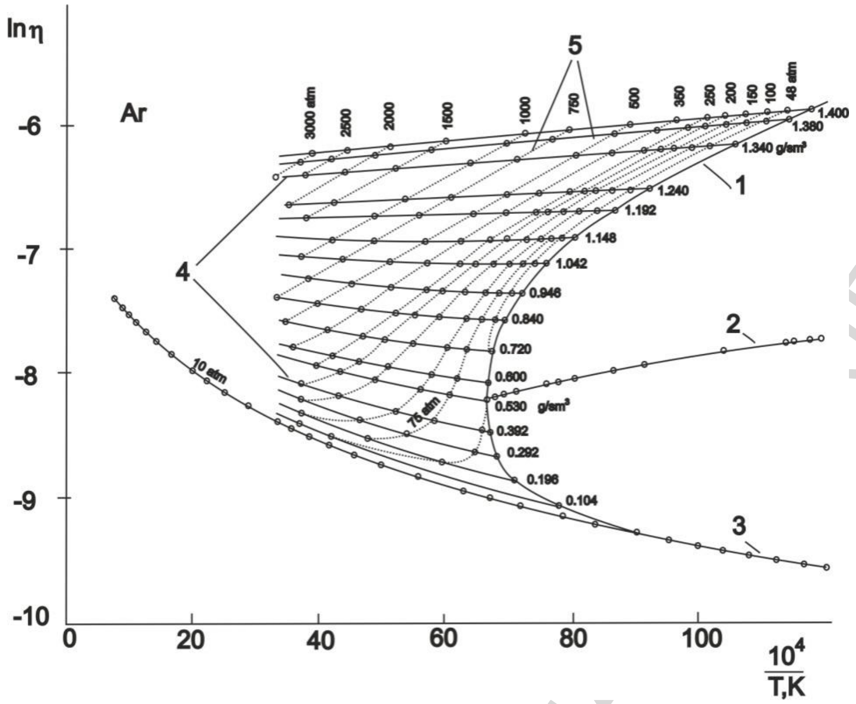

Fig.2.Temperature dependences of $\ln\eta$ versus inverse temperature $1/T$ on isochors and the coexistence curve for argon [25]: 1and 3 – liquid and vapor branches, 2 – viscosity diameter, 4 – isochors, 5 – isobars (points denote the experimental values). The solid lines are guides to the eye.

At the end of this Section we would like to note that the formula (6) can also be represented in this form:

$$\tilde{\nu}(\xi,t) \approx \xi^{1/3} \frac{(\lambda\xi_0 - 1)^{1/3}}{(\xi_0 - \xi)^{1/3}},$$

where $\xi = \eta/\eta_c$ is the ratio of the packing factor $\eta = (\pi/6)\sigma^3/\upsilon$ for arbitrary and critical points, $\xi_0 = \eta_0/\eta_c$, $\eta_0 = (\pi/6)\sigma^3/\upsilon_0$. From here it follows that the combination

$C_1(\xi) = \tilde{\nu}(\xi,t)\frac{(\xi_0 - \xi)^{1/3}}{\xi^{1/3}(\xi_0 - 1)^{1/3}}$ is expected to be close to unity for all liquid states of argon. This

combination is appropriated to compare with $C_2(\xi) = \tilde{\nu}(\xi,t)\xi^{1/3}\frac{(1-\eta_c\xi)^4}{(1-\eta_c)^4}$ following from [26],

where the main dependence of the shear viscosity upon the packing factor is derived from other reasons. The last combination in the case of its adequacy to experimental data is also to be close to unity. The behavior of $C_1(\xi)$ and $C_2(\xi)$ is presented in Fig.3.

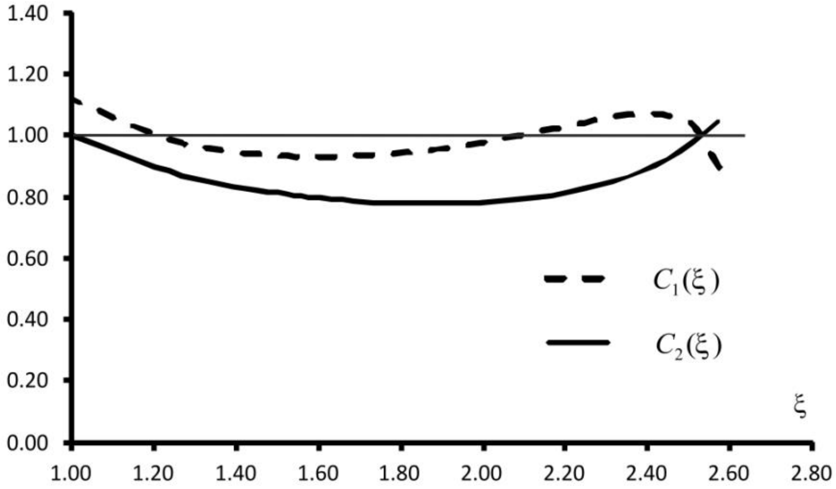

Fig.3. The dependencies of $C_1(\xi)$ and $C_2(\xi)$ vs. ξ for argon.

Our approach and that, presented in [26], are only applicable outside the fluctuation region, i.e. within the interval: $1.3 < \xi < 2.7$. The maximal deviations of both introduced combinations from unity are observed inside the interval $1 < \xi < 1.3$ where both approaches are not applicable. At the same time in the applicability region deviations of $C_1(\xi)$ from unity are lesser than $C_2(\xi)$. Here we should stress that within our approach there are two adjustable parameters: υ_0 and λ. However we can calculate their approximate values a priori with high enough accuracy: $\upsilon_0 \approx \upsilon_{tr}$ and $\lambda \approx \upsilon(T_G)/\upsilon_c$. At that, the comparison of $C_1(\xi)$ and $C_2(\xi)$ in Fig.3 is carried out for argon at $\upsilon_0 = \upsilon_{tr}$ and $\lambda \approx 0.8$. In fact, we use υ_0 and λ only for finer fitting.

IV.The similarity of kinematic shear viscosity of liquid argon, nitrogen and benzene

In this Section the main attention is focused on 1) peculiarities of the bare and averaged intermolecular potentials for all enumerated liquids; 2) properties of the kinematic shear viscosity of liquid argon which belongs to the atomic liquids with the simplest character of interparticle interactions and 3) the behavior of the kinematic shear viscosity of liquid nitrogen and benzene. Since their molecular shapes strongly differ from that of argon, it seems that their shear viscosities cannot be the same and differ from that of argon. However, due to rotation the interparticle potentials of nitrogen and benzene are undergone the self-averaging which leads to similarity of their kinematic shear viscosities.

Brief discussion of the character of the bare and averaged potentials of nitrogen and benzene as well as nitrobenzene is placed in Appendix.

Table 1. The values of ε_{LJ} ,σ, t_R , λ , ν_R , $\tilde{\upsilon}_0$, $\upsilon_0(\nu)$, $\upsilon_0(vdW)$, υ_{tr} and ζ_0 , for studied liquids.

	Ar	N_2	C_6H_6	$C_6H_5NO_2$
$\varepsilon_{LJ}/k_BT_{tr}$	1.41	0.37	1.63	3.11
σ, Å	3.405	3.55	5.25	5.59
t_R	0.997	0.987	0.996	0.972
λ	0.826	0.802	0.822	0.859
ν_R $(10^{-3} cm^2/s)$	0.519	0.61	1.18	2.761
$\tilde{\upsilon}_0$	0.461	0.446	0.421	0.304
$\upsilon_0(\nu)$, Å^3	46,50	54,94	153,35	225,34
υ_{tr}, Å^3	47,08	53,84	145,09	167,03
$\upsilon_0(vdW)$, Å^3	53,47	65,00	191,69	255,81
ζ_0	0.814	0.821	0.834	0.886

Now we are taking into account the following circumstance. The formation of the kinematic shear viscosity in liquids is mainly caused by the collective mechanism of the impulse transport. The molecular mechanism, characteristic for rare gases, is absolutely inapplicable for liquids. Here every molecule is in the field created by the nearest neighbours. Their number is more than 10. Therefore the field acting on a certain molecule is close to the average one. That is why we conclude that the kinematic shear viscosity of low molecular liquids with non-spherical molecules is mainly determined by the averaged intermolecular potential. Since the averaged potentials of nitrogen and benzene are close to the argon-like potential, we expect that their kinematic shear viscosities have argon-like character:

$$\tilde{\nu}(\upsilon, t) = \frac{\zeta_0}{(\tilde{\upsilon} - \tilde{\upsilon}_0(t))^{1/3}}, \qquad (8)$$

The correspondence between (8) and experimental data of liquid argon, nitrogen and benzene

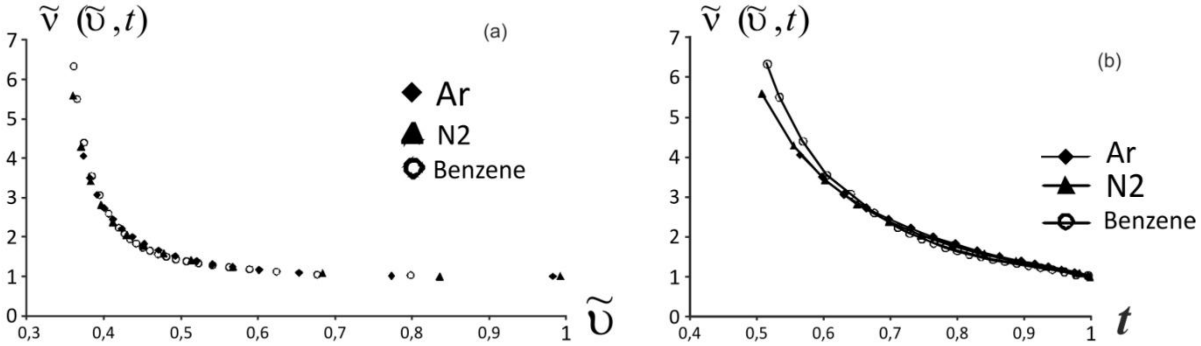

Fig.4. The similarity in the behaviour of the kinematic shear viscosities of argon, nitrogen and benzene on the specific volume (a) and temperature (b) on their coexistence curves. Experimental data are taken: argon [27], nitrogen [28], benzene [29].

are shown in the Fig.4(a). The values of ζ_0, $\tilde{\upsilon}_0$ and λ of enumerated liquids as well as for nitrobenzene (see the following Section) are collected in the Table 1. Note that for the determination of λ and $\tilde{\upsilon}_0$ it is necessary to consider the dependence of $\tilde{\nu}^3 \cdot \bar{\upsilon}$ upon $\tilde{\nu}^3$, where $\bar{\upsilon} = \dfrac{\upsilon}{\upsilon_c}$. From

$$\tilde{\nu}(\bar{\upsilon}, t) \approx \frac{(\lambda - \bar{\upsilon}_0)^{1/3}}{(\bar{\upsilon} - \bar{\upsilon}_0)^{1/3}},$$

it follows that such a dependence is to be linear: $\tilde{\nu}^3 \cdot \bar{\upsilon} = a + b \cdot \tilde{\nu}^3$, which correlates well with experimental data. Then

$$\bar{\upsilon}_0 = b, \quad \lambda = a + b\,,$$

and $\tilde{\upsilon}_0 = \frac{b}{a+b}$. As we can see, the values of $\tilde{\upsilon}_0$ and ζ_0 of liquid argon, benzene and nitrogen are very close. This allows us to attribute them to the same class of similarity.

It is necessary to note that the correspondence of their shear viscosities in variables ($\tilde{\nu}\,, t$) is expressed noticeably bad (Fig. 4(b)).

Thus, our considerations show that the kinematic shear viscosities of argon, nitrogen and benzene: 1) are mainly dependent on the specific volume, 2) have the argon-like behaviour described by the formula (8) and 3) satisfy the principle of corresponding states of all liquid states with high accuracy (parameters ζ_0 and $\tilde{\upsilon}_0$ are very close). The formula (8) can be also rewritten in the form similar to (6).

According to (8), the combination $\frac{\tilde{\nu}(\tilde{\upsilon},t)}{(1-\tilde{\upsilon}_0)^{1/3}}$ has the universal behavior for all low-molecular liquids with the averaged potentials of the Lennard-Jones type:

$$\frac{\tilde{\nu}(\tilde{\upsilon},t)}{(1-\tilde{\upsilon}_0)^{1/3}} \approx \frac{1}{(\tilde{\upsilon}-1)^{1/3}}\,.$$

V. Kinematic shear viscosity of the liquid nitrobenzene

The liquid nitrobenzene manifests two mutually contradictory properties: 1) on the one hand, its interparticle potential takes the Lennard-Jones structure, i.e. it is argon-like and 2) on the other hand, the parameters: $\zeta_0 = 0.886, \quad \tilde{\upsilon}_0 = 0.304, \quad \lambda = 0.859$ (Table 1), following from the fitting of its kinematic shear viscosity, differ noticeably from that for benzene and argon. From physical point of view, the first circumstance is more important. Therefore we conclude that the behavior of the kinematic shear viscosities for nitrobenzene and argon should be connected with each other by some symmetry transformation. It is evident, that the formula

$\tilde{\nu}(\upsilon',t)=\dfrac{\zeta'_0}{(\tilde{\upsilon}'-\tilde{\upsilon}'_0(t))^{1/3}}$ can be transformed to $\tilde{\nu}(\upsilon,t)\Rightarrow\dfrac{\zeta_0}{(\tilde{\upsilon}-\tilde{\upsilon}_0(t))^{1/3}}$ if their parameters will be connected with each other by the transformation:

$$\tilde{\upsilon}'=\tilde{\upsilon}/\mu,\quad \tilde{\upsilon}'_0=\tilde{\upsilon}_0/\mu,\quad \zeta'_0=\zeta_0/\mu^{1/3}.$$

From here it follows that

$$\tilde{\nu}(\upsilon',t)=\frac{\zeta_0}{(\mu\tilde{\upsilon}'-\tilde{\upsilon}_0(t))^{1/3}}, \tag{9}$$

where $\mu=\tilde{\upsilon}_0/\tilde{\upsilon}'_0\approx 1.38$, is equivalent to the initial expression for the kinematic shear viscosity of nitrobenzene. The Fig.7 illustrates the full coincidence of the kinematic shear viscosity of nitrobenzene (NB) calculated according to (9) to that for benzene (B).

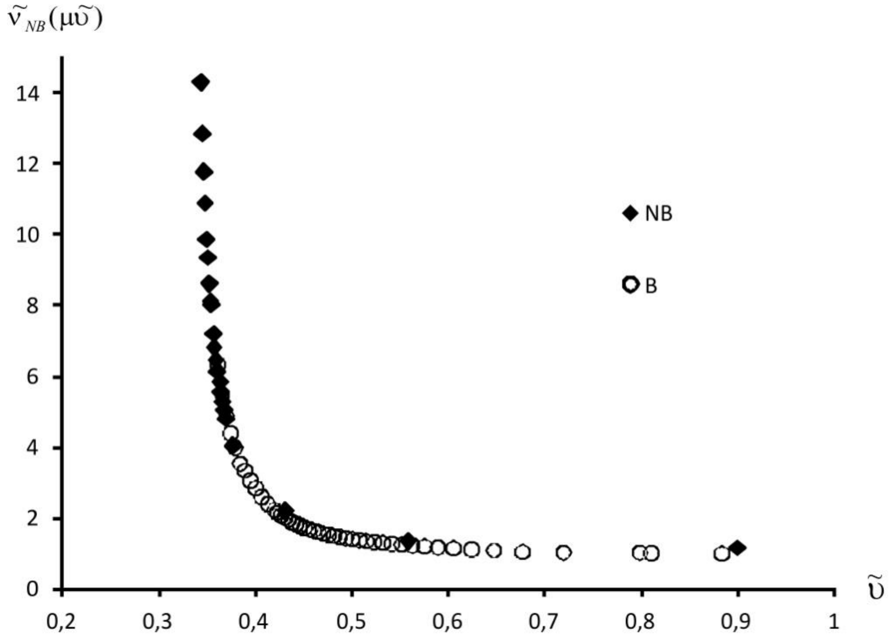

Fig.5. Comparative behaviuor of the kinematic shear viscosities of benzene and nitrobenzene.

Thus, we can conclude that the shear viscosities of nitrogen as well as benzene and nitrobenzene can be obtained from the argon kinematic shear viscosity by suitable similarity transformations.

The significant difference of $\lambda'_{eff}=\lambda'/\mu\approx 0.62$ from unity testifies on the strong dimerization near the critical point.

VI. The similarity principle of corresponding states

Let us reformulate the results obtained above in more suitable form. For this we rewrite the formula (6):

$$\tilde{\nu}(\tilde{\upsilon},t) \approx \frac{(\tilde{\upsilon}_R - 1)^{1/3}}{(\tilde{\upsilon} - 1)^{1/3}} \quad \text{or} \quad \tilde{\nu}(\upsilon,t) \approx \frac{(\upsilon_R - \upsilon_{tr})^{1/3}}{(\upsilon - \upsilon_{tr})^{1/3}}, \qquad (10)$$

where $\tilde{\upsilon} = \upsilon / \upsilon_{tr}$ and $\tilde{\upsilon}_R = \upsilon_R / \upsilon_{tr}$, υ_{tr} is the specific volume at the triple point. Here, we took into account that υ_0 practically coincides with the specific volume at the triple point.

If two liquids belong to the same similarity class, i.e. their molecular parameters transforms to each other by means of $\mu-$transformation, we have:

$$\frac{\upsilon - \upsilon_{tr}}{\upsilon_R - \upsilon_{tr}} = \frac{\upsilon' - \upsilon'_{tr}}{\upsilon'_R - \upsilon'_{tr}}$$

and

$$\tilde{\nu}(\upsilon,t) = \tilde{\nu}'(\upsilon',t)\,.$$

So, the kinematic shear viscosities of two isomorphic liquids are connected with each other by the relation:

$$\tilde{\nu}'(\upsilon',t) = \tilde{\nu}(1 + \kappa(\upsilon' - 1),t), \quad \kappa = \frac{\tilde{\upsilon}_R - 1}{\tilde{\upsilon}'_R - 1}\,. \qquad (11)$$

It is the final form of the similarity principle of corresponding states of liquids.

The consistency of experimental data on the shear viscosity of all liquids, enumerated above, with (11) are presented in the Fig.6.

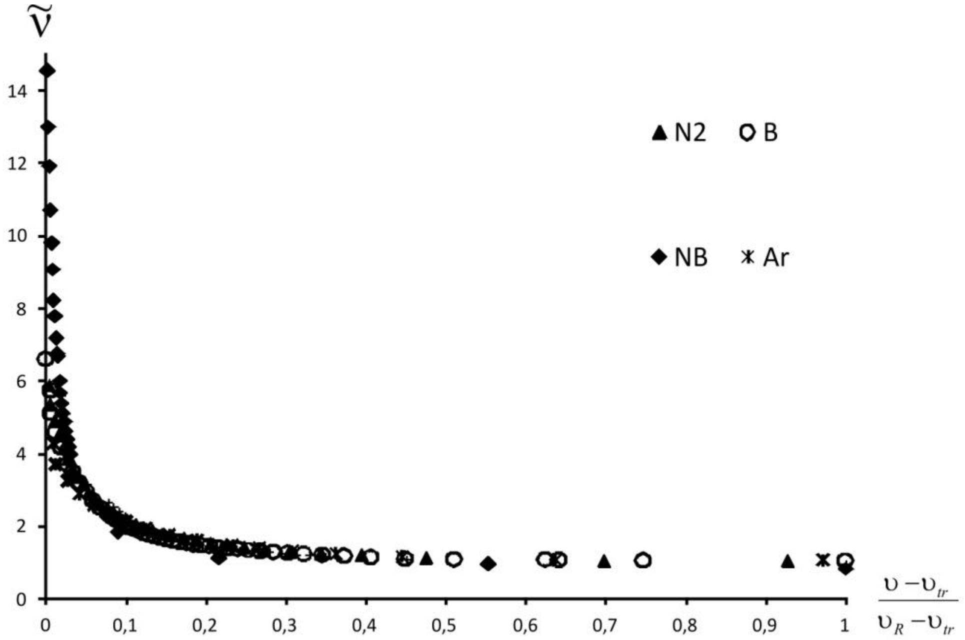

Fig.6. Experimental values of the kinematic shear viscosity of argon, nitrogen, benzene and nitrobenzene are got with the help of (11).

It is necessary to note that the transformation

$$\upsilon' \to 1+\frac{1}{\kappa}(\upsilon-1),t), \quad \kappa=\frac{\tilde{\upsilon}_R-1}{\tilde{\upsilon}'_R-1},$$

inverse to that used in (11), allows us to transform the kinematic shear viscosity from a range $(1<\tilde{\upsilon}'<\tilde{\upsilon}'_R)$ to another range $(1<\tilde{\upsilon}<\tilde{\upsilon}_R)$:

$$\nu'(1+\frac{1}{\kappa}(\tilde{\upsilon}-1),t) \Rightarrow \nu(\tilde{\upsilon},t)\,.$$

In connection with this we want to stress that 1) the behaviour of the kinematic shear viscosity of molecular liquids with the similar averaged potential is described by the same function, and 2) this function can be defined in some fixed interval: $1 \le \tilde{\upsilon} < \tilde{\upsilon}_R$. Therefore, unlike the standard formulation of the similarity principle [30], the fraction volume is normalized on the volume at the triple point (instead of the normalization on the critical value).

On the coexistence curve $\tilde{\upsilon}=\tilde{\upsilon}(t)$, therefore the kinematic shear viscosity equals to

$$\frac{\tilde{\nu}_{CC}(t)}{(\tilde{\upsilon}_R - 1)^{1/3}} = \frac{1}{(\tilde{\upsilon}(t) - 1)^{1/3}}\,,\ t = T / T_{tr}\,.$$

Discussion of the results obtained

The main results of this paper state to the following: 1) the behaviour of the kinematic shear viscosity of argon is mainly determined by the packing factor similar to that of the van der Waals equation of state; 2) the low-molecular liquids with nonspherical molecules show the argon-like behavior of their shear viscosities, i.e. they belong to the same similarity class; 3) similar behavior of low-molecular liquids is caused by the identical behavior of their averaged interparticle potentials, having the Lennard-Jones form; 4) a new formulation of the similarity principle as well as new definition of corresponding states are given.

The contrast between the standard [30], and new formulations of the similarity principle is also manifested in the behavior of thermodynamic quantities, in particular, in universality of the coexistence curves of low-molecular liquids in the variables: $\frac{\upsilon - \upsilon_{tr}}{\upsilon_R - \upsilon_{tr}}$ and $\frac{T - T_{tr}}{T_R - T_{tr}}$. In this case the similar behavior is observed in all liquid states: from the triple point up to the critical one (in the standard variables only in the vicinity of the critical point).

The equivalency of argon having spherical atoms and liquids with non-spherical molecules of benzene type is caused by the rotation of their molecules. Due to this, non-spherical molecules behave as quasi-spherical particles. The model of viscous motion, we propose, shows the role of the packing effects (excluded volume) in the formation of the shear viscosity. As we can see, the values of the excluded volume corresponding to the shear viscosity are rather close to those obtained from the van der Waals equation of state [31] (see Table 1).

The expression (9) for the kinematic shear viscosity of low-molecular liquids reproduces their experimental values with quite satisfactory accuracy. The characteristic deviations do not exceed 10%. The deviations can reach 15% only in narrow temperature intervals near the critical point. To improve the agreement between theoretical and experimental data we can consider that excluded volume depends on temperature. In this case

$$\tilde{\nu}(\upsilon,t) \approx \frac{\zeta_0}{(\tilde{\upsilon}-\tilde{\upsilon}_0)^{1/3}}(1+\frac{1}{3}\frac{\delta\tilde{\upsilon}_0(t)}{(\tilde{\upsilon}-\tilde{\upsilon}_0)}+..)\,.$$

The temperature dependencies of $\delta\tilde{\upsilon}_0(t)$ of argon, benzene and nitrogen are presented in Fig.7. In fact, the description of $\delta\tilde{\upsilon}_0(t)$ requires the further development of our study.

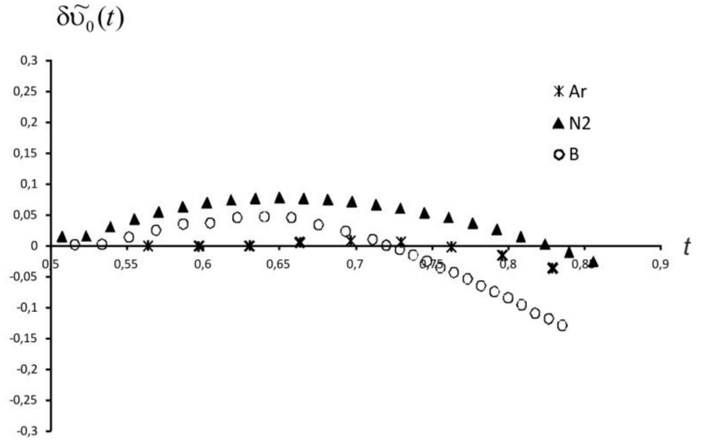

Fig.7. Small deviations of the excluded volume from their fixed values.

It is necessary to stress, that only small distinctions in values of $\tilde{\upsilon}_0$ lead to deviations from the similarity principle. The values of ζ_0 are not independent, they are connected with $\tilde{\upsilon}_0$. It is very important that our approach has no adjustable parameters in the zero approximation. The parameters υ_0 and λ are used us only for finer fitting. Closeness of these parameters for different liquids (see Table 1) does not abandon doubts in the applicability of the similarity principle for the description of the kinematic shear viscosity.

The deviation of the kinematic shear viscosity from the argon-like behavior is expected only for rather low temperatures at which the orientation correlations become essential. The most contribution to the orientation correlations is caused by dipole-dipole interactions. Among liquids, examined in our paper, only nitrobenzene molecules have dipole moments. By order of magnitude, the dipole correlations will be important only at temperatures: $T/T_c < t_d$, where $t_d \sim \frac{\vec{D}^2}{3k_B T_c < r_{12}^3 >}$ is the characteristic temperature of dipole ordering. Taking into account that $\frac{1}{< r_{12}^3 >} \approx n$, where n is the numerical density, we find $t_d \approx 0.4$. We note that the reduced triple temperature of nitrobenzene is practically the same ($t_{tr} \approx 0.39$). It means that the noticeable deviations in the argon-like behaviour are expected only in supercooled states of nitrobenzene. The similar situation is also expected in supercooled water.

At the same time the influence of quadrupole ordering is essentially smaller. For corresponding characteristic temperature we find $t_Q \sim \frac{Q^2}{3k_B T_c < r_{12}^5 >} \approx (0.04 \div 0.1)$.

The study of the kinematic shear viscosity of water will be given in a separate paper. We will show that ν_w is mainly the combination of 1) exponential contribution characteristic of activation theory [1-3] and 2) argon-like contribution. The first of them is dominating for $T/T_c < t_d$ that is inherent for supercooled states of water and the second one corresponds to practically all normal states of liquid water.

We cordially thank Professor H. Hasse and Dr. Ya.Vrabec for the discussion of our ideas in time of their appearance.

Appendix

Here we want to discuss the most characteristic peculiarities of the bare intermolecular potentials for nitrogen as well as for benzene and nitrobenzene. Due to this we will be able to understand better the role of interactions which depends on the molecular orientations. They stimulate the weak dimerization, that is especially important near the critical point.

a) Interaction of nitrogen molecules

The starting potential for nitrogen molecules takes the form:

$$\Phi(1,2) = \Phi_R(1,2) + \Phi_D(1,2) + \Phi_Q(1,2)\,, \tag{A1}$$

where $\Phi_R(1,2)$ describes the repulsive interaction, $\Phi_D(1,2)$ is the dispersive part of the interparticle potential and

$$\Phi_Q(1,2) = \frac{3}{4}\frac{Q^2}{r_{12}^5}\left[3 + 35(\vec{n}_1\vec{e}_r)^2(\vec{n}_2\vec{e}_r)^2 - 5\left((\vec{n}_1\vec{e}_r)^2 + (\vec{n}_2\vec{e}_r)^2 + 4(\vec{n}_1\vec{e}_r)(\vec{n}_2\vec{e}_r)\right)\right], \tag{A2}$$

is the term describing the quadrupole-quadrupole interaction between nitrogen molecules, $\vec{n}_1$ and $\vec{n}_2$ are the orts directed along molecular axes, and $\vec{e}_r = \vec{r}/r$. Relatively simple expression for $\Phi_D(1,2)$ is presented in [32]. Its more detailed description is given in [33]. However, the relative value of the difference between them in typical configurations of two nitrogen molecules does not exceed (2-3)%. Therefore, in our calculations we are going to use the expression from [32].

Rigorously speaking, the first two terms in (A1) are also dependent on angles. However the angular dependence of $\Phi_R(1,2)$ is only manifested on small distances corresponding to intermediate contact of nitrogen molecules. The angular part of the dispersive contribution $\Phi_D(1,2)$ is caused by fluctuation of quadrupole interactions. It reduces with distance by power

law: $\sim 1/r_{12}^8$, as well as the direct quadrupole-quadrupole interaction. However the last contribution is essentially more. These facts are supported by the direct calculations in accordance with the model expression for $\Phi_D(1,2)$ in [32]. It means that the relative angular disposition of nitrogen molecules is mainly determined by quadrupole interaction.

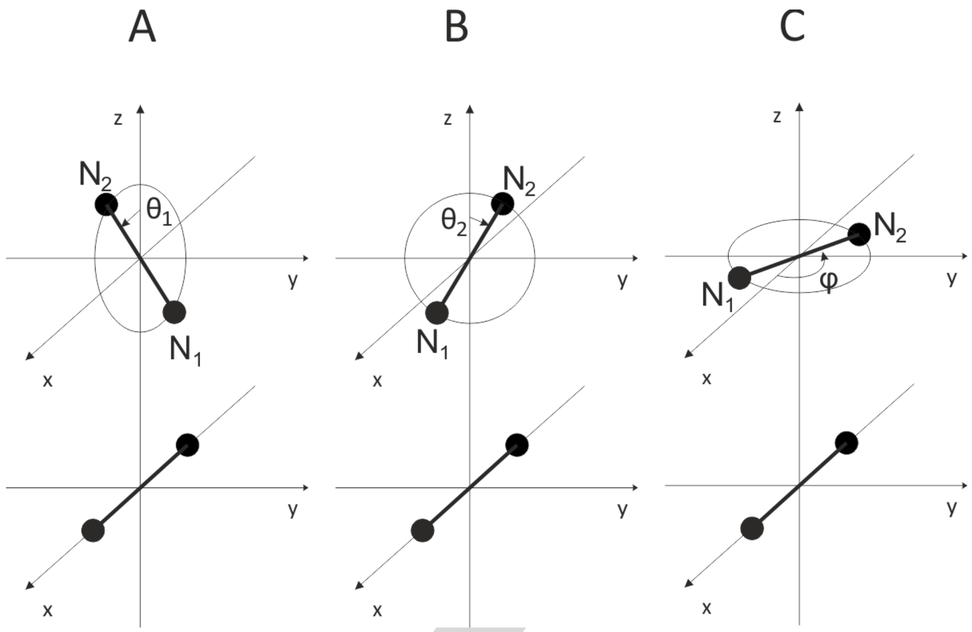

Fig.A1. Characteristic configurations of two nitrogen molecules (they correspond to rotations in the planes: (*xz)* - A, (yz) – B and (xy) – C).

The analysis of the interparticle interactions for configurations in Fig. A1 shows: 1) the minimum of the dispersive interaction energy is observed for $\vec{n}_1 \parallel \vec{n}_2$ and 2) the minimum of the interaction energy caused by dispersive and direct quadrupole-quadrupole interactions corresponds to $\vec{n}_1 \perp \vec{n}_2$ for all distances between centers of mass of nitrogen molecules.

Thus, we can conclude that the lowest value of the full interaction energy corresponds to the configuration where the upper molecule is directed along the OZ-axis ($\theta_1 = \theta_2 = 0$). This result is consistent with that in [33].

However, the ground state energy of dimer is smaller than the thermal energy of molecules. Therefore the degree of dimerization is slighting in liquid nitrogen practically in the whole range of its liquid states. Nitrogen molecules rotate almost freely at all these temperatures. The dimerization degree increases [17] only near the critical point because the specific volume, accessible for a dimer, becomes several times bigger. It is necessary to note that the dimerization of molecules influences on the width of the fluctuation region, i.e. on the value of λ .

For the further discussion it is important that the interaction between benzene molecules is fully analogous to that between nitrogen ones (see (A1) and (A2), where the orts $\vec{n}_1$ and $\vec{n}_2$ are normal to benzene ring.

The bare potential of nitrobenzene molecules additionally includes the dipole-dipole contribution:

$$\Phi_{NB}(r,\Omega_1,\Omega_2) = \Phi_{CB}(r,\Omega_1,\Omega_2) + \frac{D^2}{r^3}\left(\vec{n}_1\cdot\vec{n}_2 - 3(\vec{n}_1\vec{e}_r)(\vec{n}_2\vec{e}_r)\right) + \ldots,$$

where the first term is close to that of benzene molecules [34-36] ($\vec{n}_i$, $i = 1,2$, are the orts determining directions of dipole moments for molecules, D is the modulus of dipole moment of nitrobenzene molecule). The term $\Phi_{CB}(r,\Omega_1,\Omega_2)$ causes the disposition of nitrobenzene molecules in mutually perpendicular planes like it happens with benzene molecules. However the stronger dipole-dipole interaction changes this situation. Due to this the dipole moments of nitrobenzene molecules become antiparallel while the centers of mass of molecules displace relatively to each other. As a result the perpendicular disposition of molecular rings becomes unstable and they pass to parallel disposition. This mechanism of the dimerization of nitrobenzene molecules is described in details in [37]. Since the dimerization degree of nitrobenzene in its liquid state is rather large (up to 0.9 in accordance with [37]) we expect that the value of λ will be essentially different from unity.

b) Averaged intermolecular potential

Being far away from the critical point nitrogen molecules rotate thermodynamically that is why many kinetic properties of liquid nitrogen are determined by the averaged potential $U_a(r)$. It is determined by the expression:

$$\exp\left(-\beta U_a(r_{12})\right) = \oint\limits_{\Omega_1=4\pi}\frac{d\Omega_1}{4\pi}\oint\limits_{\Omega_2=4\pi}\frac{d\Omega_2}{4\pi}\exp\left(-\beta\Phi(1,2)\right) \equiv <\exp\left(-\beta\Phi(1,2)\right)>, \qquad \text{(A3)}$$

Thus, in binary approximation the bare and averaged potentials lead to the same configuration integrals and the free energies.

To illustrate the result of the averaging in accordance with (A2) let us consider the averaging procedure on the base of: $|\beta\Phi(1,2)| << (<) 1$. Here we can expand $\exp(-\beta\Phi(1,2))$ in the series and we can average each term independently:

$$< \exp(-\beta\Phi(1,2)) > \Rightarrow 1 - \beta\Phi_0(r_{12}) + \frac{1}{2}\beta^2\Phi_0^2(r_{12}) + \frac{1}{2}\beta^2 < \Phi_A^2(r_{12},\Omega_1,\Omega_2) > + \dots, \qquad \text{(A4)}$$

where $\Phi(1,2)$ is supposed to be equal:

$$\Phi(1,2) = \Phi_0(r_{12}) + \Phi_A(r_{12},\Omega_1,\Omega_2).$$

Additionally it is supposed that the angular parts of the interparticle potential satisfy the equations:

$$< \Phi_A(r_{12},\Omega_1,\Omega_2) > = < \Phi_A^3(r_{12},\Omega_1,\Omega_2) > = \dots = < \Phi_A^{2k+1}(r_{12},\Omega_1,\Omega_2) > = \dots = 0.$$

Representing the right side of (A4) in the exponential form we get

$$< \exp(-\beta\Phi(1,2)) > \Rightarrow \exp(-\beta(\Phi_0(r_{12}) - \frac{1}{2}\beta < \Phi_A^2(r_{12},\Omega_1,\Omega_2) > + ..)),$$

which is the cumulant representation of the average of exponent [38]. This way we get that

$$U_a(r_{12}) = \Phi_0(r_{12}) - \frac{1}{2}\beta < \Phi_A^2(r_{12},\Omega_1,\Omega_2) > + \dots . \qquad \text{(A5)}$$

In this case the standard average has the structure:

$$U^{(a)}(r_{12}) = \frac{< \Phi(1,2)\exp(-\beta\Phi(1,2)) >}{< \exp(-\beta\Phi(1,2)) >} \Rightarrow \Phi_0(r_{12}) - \beta < \Phi_A^2(r_{12},\Omega_1,\Omega_2) > + \dots \qquad \text{(A6)}$$

Thus, the difference between $U_a(r_{12})$ and $U^{(a)}(r_{12})$ is connected with the contributions generated by the angular part of the interparticle potential.

To carry out the integration over the angular variables one can use any representation, in particular, the expansion of $\Phi_A(r_{12},\Omega_1,\Omega_2)$ in the series on the spherical functions.

In general case the cumulant expansion of $<\exp\left(-\beta\Phi(1,2)\right)>$ is correct only for rather long distances between molecules. If the intermolecular distance is small the corresponding averaging can be produced by numerical methods.

The detailed analysis shows that $U_a(r)$ for nitrogen, benzene and nitrobenzene molecules takes the Lennard-Jones form (Fig.A2).

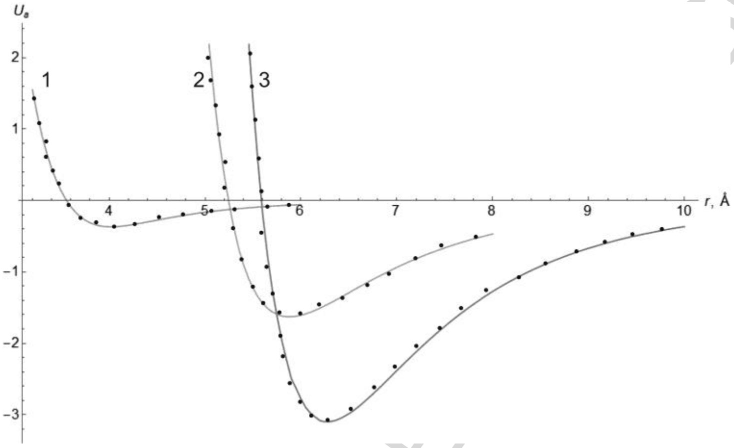

Fig. A2. The averaged potential between nitrogen (1), benzene (2) and nitrobenzene (3). Dots denote the values calculated according to (A3), solid lines correspond to fitting with the help of the Lennard-Jones potential.

References

[1] D.Eisenberg and V. Kauzmann, *The Structure and Properties of Water*; Oxford University Press, New York, USA, 1969.

[2] Byung Chan Eu, *Transport Coefficients of Fluids*; Berlin ; London : Springer, 2011.

[3] J.P. Hsu and S.H. Lin. Temperature dependence of the viscosity of nonpolymeric liquids. *J. Chem. Phys*. **2003**,118, 172-178, DOI: 10.1063/1.1525282.

[4] J. Frenkel. *Kinetic Theory of Liquids*; Dover Publ., New York, USA,1955.

[5] E. N. da C. Andrade. The Viscosity of Liquids. Nature.1930, 125, 309-310, DOI: 10.1038/125309b0.

[6] V.Blazhnov, N.P. Malomuzh, S.V. Lishchuk. Temperature dependence of density, thermal expansion coefficient and shear viscosity of supercooled glycerol as a reflection of its structure. *J. Chem. Phys*.**2004**, 121, 6435-6441,DOI: 10.1063/1.1789474.

[7] H.R. Pruppacher. Self-Diffusion Coefficient of Supercooled Water. *J. Chem. Phys*. **1972**, 56,101-107, DOI: 10.1063/1.1676831.

[8] K. Yao M.Okada, Y.Hiejima, H.Kohno and Y.Kojihara. Dielectric relaxation of water and heavy water in the whole fluid phase.*J. Chem. Phys*. 1999, 110, 3026-3036. DOI: 10.1063/1.477897.

[9] N.P.Malomuzh, V.N. Mahlaichuk, P.V. Mahlaichuk, K.N.Pankratov. Cluster structure of water in accordance with the data on dielectric permittivity and heat capacity. *J. Str. Chem. (Russia*). **2013**, 54, S24-S39.DOI: 10.1134/S0022476613080039.

[10] L.D. Eicher, B.J. Zwolinski. High-precision viscosity of supercooled water and analysis of the extended range temperature coefficient.*J. Phys. Chem*.**1971**,75, 2016–2024,DOI: 10.1021/j100682a019.

[11] C. A. Angell. Supercooled Water**.** *Ann. Rev. Phys. Chem*. **1983**,34,593-630. DOI: 10.1146/annurev.pc.34.100183.003113.

[12] Fisher I.Z. *Statistical Theory of Liquids*. University of Chicago Press, 1964.

[13] Vrabec Jadran, Jürgen Stol, Hans Hasse. A Set of Molecular Models for Symmetric Quadrupolar Fluids *The Journal of Physical Chemistry B*, **2001**, 105.48, 12126-12133, DOI: 10.1021/jp012542o.

[14] R.Casalini, C.M.Roland. An equation for the description of volume and temperature dependences of the dynamics of supercooled liquids and polymer melts. *J.Non-Cryst. Sol.***2007**, 353(41–43),3936–3939.DOI:10.1016/j.jnoncrysol.2007.03.026.

[15] A.Z. Patashinskii, V.L. Pokrovskii.*Fluctuation Theory of Phase Transitions*. Pergamon Press,1979.

[16] M. Nishio. The CH/π hydrogen bond in chemistry. Conformation, supramolecules, optical resolution and interactions involving carbohydrates. *Phys. Chem. Chem. Phys*. **2011**,13, 13873-13900, DOI**:** 10.1039/C1CP20404A.

[17] V.L.Kulinskii, N.P.Malomuzh. Dipole fluid as a basic model for the equation of state of ionic liquids in the vicinity of their critical point.*Phys.Rev.E*.**2003**, 67**,** 011501-1 – 011501-8. DOI: 10.1103/PhysRevE.67.011501.

[18] M.D.Dolgushin,V.M.Pinchuk. Theoretical study of the nature of the hydrogen bond by comparative calculations .(ITF-76-49P, 1976).

[19] P.Barnes. In *Progress in Liquid Physics*, ed. Croxton C.A. Wiley,Chichester, England, 1978.

[20] R. L. Fulton , P. Perhaes. Sharing of Electrons in Molecules: Characterization of Hydrogen Bonds. *J. Phys. Chem. A*.**1998,**102, 9001-9020.DOI: 10.1021/jp9821228.

[21] Weeks J.D., Chandler D., Andersen H.C. Role of Repulsive Forces in Determining the Equilibrium Structure of Simple Liquids.*J.Chem.Phys*.**1971**, 54, № 12, 5237-5246.DOI: 10.1063/1.1674820.

[22] N.P. Malomuzh, V.P. Oleynik. Nature of the kinematic shear viscosity of water.*J. Struct. Chem. (Russia)*. **2008**,49**,** N 6, 1055-1063, DOI:10.1007/s10947-008-0178-1.

[23] L.A.Bulavin, A.I.Fisenko, N.P.Malomuzh. Surprising properties of the kinematic shear viscosity of water. *Chem.Phys.Lett*.**2008**, 453, 183-187, DOI:10.1016/j.cplett.2008.01.028.

[24] A.Batchinski. Untersuchungenüber die innereReibung der Flussigkeiten. *Z.Phys.Chem*. **1913**, 84**,** 643-706.

[25] V.P. Slusar, N.S. Rudenko, V.M. Tretyakov. *Ukr.J. Phys*.**1972**, 17, 1257-1268 .

[26] N.Ohtori, Y.Ishii. Explicit expression for the Stokes-Einstein relation for pure Lennard-Jones liquids.*Phys. Rev. E***2015**, 91, 012111.DOI: 10.1103/PhysRevE.91.012111.

[27] B.A. Younglove, H.J.M. Hanley. The Viscosity and Thermal Conductivity Coefficients of Gaseous and Liquid Argon. *J. Phys. Chem. Ref. Data*. **1986**, 15,1323-1338, DOI: 10.1063/1.555765.

[28] R.Span, E.W. Lemmon, R.T. Jacobsen,W.Wagner, A.Yokozeki. A Reference Equation of State for the Thermodynamic Properties of Nitrogen for Temperatures from 63.151 to 1000 K and Pressures to 2200 MPa. *J.Phys. Chem. Ref. Data.* **2000**, 29, 1361-1434,DOI: 10.1063/1.1349047.

[29] N.B. Vargaftik. *Handbook of Physical Properties of Liquids and Gases*.2nd Edition. Hemisphere Publishing Corp., Washington, 1975.

[30] Croxton C.A. *Liquid State Physics.A Statistical Mechanical Introduction.*

Cambridge: Cambridge University Press, 1974.

[31] B. P. Nikolsky. *Guide-Book for Chemist (in Russian).*Chemistry, Moscow, 1964.

[32] J.Vrabec, J.Stoll, H.Hasse. A Set of Molecular Models for Symmetric Quadrupolar Fluids. *J. Phys. Chem. B,* **2001**, *105* (48), pp 12126–12133**.**DOI:10.1021/jp012542o

[33] P. Strąk , S. Krukowski. Molecular nitrogen-N2 properties: The intermolecular potential and the equation of state. *J. Chem. Phys.* **2007**, 126, 194501. DOI: 10.1063/1.2733651

[34] E. Wilhelm, R.Battino. Estimation of Lennard-Jones (6,12) Pair
Potential Parameters from Gas Solubility Data. *J. Chem. Phys.***1971**, 55, 4012;
DOI: 10.1063/1.1676694.

[35] M Sliwinska-Bartkowiak. The second virial coefficient for critical mixtures of o-nitrotoluene with alkanes and formally similar systems. *J. Phys.: Condens. Matter* , **1993**,5**,** 407-422.

[36] Do Duong. Adsorption Science and Technology: Proceedings of the Second Pacific Basin Conference on Adsorbtion Science and Technology. World Scientific, **2000** – p. 740.

[37]. Toshiyuki Shikata, Yuji Sakai, and Junji Watanabe. Nitrobenzene anti-parallel dimer formation in non-polar solvents. AIP Advances , **2014**, 4, 067130 - 067130-12, (); doi:10.1063/1.4884393

[38] Isihara A. *Statistical Physics*. Academic Press, New York – London, 1971.

Highlights

- Kinematic shear viscosity for argon is mainly determined by the packing factor.
- The low-molecular liquids show the argon-like behavior of their shear viscosities.
- There is a new formulation of the similarity principle for corresponding states .