QUALITATIVE PROPERTIES
OF THE SHEAR VISCOSITY OF LIQUIDS

In this paper, two theses are substantiated. (i) The viscosity of liquids in the larger part of the temperature interval, where this phase state exists, is governed by frictional effects between the molecular layers that move relative to one another. (ii) Argon and water at temperatures $T_H < T < T_C$ ($T_H \approx 315$ K and $T_C$ is the corresponding critical temperature) have kinetic coefficients belonging to the same class of similarity. This is so because the behavior of the shear viscosity in water is driven by the averaged interaction potential between the molecules. On the basis of the similarity principle applied to the corresponding states of water and argon, the self-diffusion and shear viscosity coefficients of water are calculated. The inadequacy of activation mechanisms responsible for the formation of the viscosity and self-diffusion processes in water and most low-molecular liquids is discussed.

Keywords: self-diffusion coefficient, water viscosity.

1. Introduction

There are many publications, where the nature of the shear viscosity in liquids was studied (see, e.g., works [1–10]). However, there is no ultimate viewpoint on this issue. It is so because the temperature intervals are rather narrow in many cases, and a distinct choice among the formulas of various types is not an easy task. Bearing all that in mind, in this paper, an attempt is made to formulate clear qualitative criteria for the applicability of that or another approach. Most attention is focused on the qualitative comparison between the Batchinski formula [11] and the formula that describes the shear viscosity of liquids in the framework of our approach [12] and which is, to some extent, similar to the former. The Batchinski formula was proposed on the basis of ideas that were used by Van der Waals (VdW), when constructing his equation of state. From this point of view, it seems that this formula should possess a universal character. In our case, the main assumptions are based on a thorough analysis of the thermal motion of molecules in liquids and the mechanisms of momentum transfer between the layers that move relative to one another. We would like to emphasize that the solution of any problem can be considered complete if a detailed microscopic theory of the phenomenon has been developed. However, in our cases, these are phenomenological theories, for which a clear physical meaning of involved quantities is extremely important.

Not less important is a critical analysis of the widespread application of formulas derived in the framework of ideas associated with activation mechanisms. This issue is not new. It has been discussed in plenty of works [13–17]. The inapplicability of activation theories to the description of the shear viscosity in argon and other atomic liquids seems to be generally recognized. But the properties of water and, especially, alcohols differ from those of argon very
much. Therefore, just those substances seem to be objects of the activation approach. In any case, the clear formulation criteria are required in order to unambiguously resolve this issue.

There is another general point that repeatedly prompts us to deal with the origin of the shear viscosity in various liquids. This is the similarity principle for the corresponding states of liquids. A basis for the similarity of thermodynamic liquid states is the VdW equation. It satisfactorily describes the thermodynamic properties of gases, and qualitatively correctly the properties of liquids. In particular, it brings us to a conclusion that the coexistence curves are similar for liquids that differ significantly from one another by the form of the interaction potential between the molecules [18–20]. For instance, water and alcohols possess argon-like properties. The physical basis of this similarity lies in that they are governed by the averaged potentials of intermolecular interaction, the latter having the same structure of the Lennard-Jones potential in both water and argon.

Analogously, one may expect that the properties of the shear viscosity are also determined by the averaged potentials. Really, the shear viscosity emerges as a result of the friction between the molecular layers, when they move relatively slowly with respect to one another. The relevant characteristic time corresponds to a layer displacement by an intermolecular distance, and this quantity is much longer than the time required to change the intermolecular orientation. That is why the friction magnitude has to be determined by the properties of averaged potentials.

In this work, a few qualitative arguments are formulated. They allow one to clearly distinguish the Batchinsky and our approaches. They demonstrate that the averaged character of the molecular thermal motion in water is similar to that in argon, i.e. the shear viscosity of liquid water has an argon-like behavior within almost the whole temperature interval of this phase. Finally, the applicability of the similarity principle to the calculation of the shear viscosity of water is discussed.

2. Self-Consistency Criteria for Shear Viscosity Formula

In works [12, 18, 21–23], it was shown that the shear viscosity of low-molecular liquids is a result of the friction between the surfaces of molecular layers (see Fig. 1).

Note that the mechanism of viscosity formation in liquids is mainly the “friction” of molecular layers rather than the transfer of the momentum of a molecule that transits from one layer to another, as it occurs in dense gases. Molecules in liquids cannot transit from one layer to another because of the lack of a sufficient free volume (see below). In works [12, 18], it was shown that the shear viscosity of argon and all low-molecular liquids looks like

\[
\bar{\nu}(\tilde{v}, t) \approx \frac{\zeta_i}{(\tilde{v} - \bar{v}_0(i))^3/3}, \\
\zeta_i = (1 - \bar{v}_0(i))^{1/3}, \quad i = Ar, w, ..., 
\]

where \(\bar{\nu}(t) = \nu(t)/\nu_tr\); \(\nu_tr\) is the kinematic shear viscosity at the triple point; \(t = T/T_tr\) and \(\tilde{v} = v/\nu_tr\) are the dimensionless temperature and specific volume, respectively; \(T_tr\) and \(\nu_tr\) are the temperature and specific volume, respectively, at the triple point; \(\bar{v}_0(i) = v_0(i)/\nu_tr\); and \(v_0(i)\) is the excluded volume of the system corresponding to its shear viscosity. This formula describes well the shear viscosity in all liquids, for which the averaged intermolecular potential is similar to the Lennard-Jones potential in argon.

The temperature dependences of the self-diffusion coefficient and the shear viscosity in liquids are usually described by an expression containing one or a few exponential terms [1–3]:

\[
\eta = \eta_1 \exp(E_{a1}/k_B T) + \eta_2 \exp(E_{a2}/k_B T) + ..., 
\]

where \(\eta\) is the shear viscosity, and \(E_a\) the activation energy. In work [12], it was shown that formula (1) reproduces the shear viscosity of such liquids as benzene, nitrobenzene, nitrogen, liquid alkaline [24], as well as transition metals [25], with a high accuracy. In work [22], it was shown that formula (2) also describes well the shear viscosity of water in almost the whole temperature interval of its existence in the
liquid state, 315 K < T < 620 K. At temperatures below 315 K, the character of the thermal motion of water molecules becomes complicated, and the behavior of the shear viscosity changes [18].

According to Batchinski [11], the shear viscosity is described by the expression

\[ \nu(\tilde{v}, t) = \frac{\zeta_i}{\tilde{v} - \tilde{v}_0^{(i)}} \]  

where the denominator is similar to one of the terms in the VdW equation of state. Batchinski also determined the excluded volume \( \tilde{v}_0^{(i)} \), which turned out different from, although close to, the excluded volume in the VdW equation. In our case, the value of excluded volume differed from the value of specific volume at the triple point in the third digit after the decimal point. Therefore, we will consider the equation

\[ \nu(\tilde{v}, t) = \frac{\zeta_i}{(\tilde{v} - \tilde{v}_0^{(i)})^\xi} \]  

with an arbitrary power exponent \( \xi \). This formula corresponds to the smallest deviations of

(i) the normalized shear viscosity from the experimental data (the parameter \( 1 - R_x^2 \)),

(ii) the quantity \( \tilde{v}_0^{(i)} \) from unity (i.e. the excluded volume from its value at the triple point), and

(iii) the parameter \( \zeta_i^{1/\xi} \) from \( (1 - \tilde{v}_0^{(i)}) \).

Note that all indicated criteria of the theoretical approach adequacy are mutually independent. Really, a minimum value of the parameter \( R^2 \) does not guarantee that the value of \( \tilde{v}_0^{(i)} \) is close to 1, which has to be owing to its physical meaning. Concerning the necessity of item (iii), it is dictated by the requirement that formula (1) should be self-consistent at the triple point.

The values of all experimental and calculation parameters for the shear viscosity of argon are quoted in Table 1. In the table, the quantity \( R_x^2 \) is the relative mean square difference between the experimental and calculated parameters. One can see that

(i) the smallest deviations of the quantity \( 1 - R_x^2 \) from 1 are mainly observed at \( \xi = 1/3 \), and

(ii) the values of the normalized excluded volume are the closest to 1 in the case \( \xi = 1/3 \).

From the physical viewpoint, this conclusion is extremely important, because the specific volume of the system at the triple point should be considered as a physically substantiated estimate of the excluded volume. A value of 1/5 for the power exponent \( \xi \) has no physical sense, because the corresponding values of the own volume exceed 1. The differences between \( \zeta_i^{1/\xi} \) and \( 1 - \tilde{v}_0 \) fall within the experimental error interval; therefore, formula (1) should be considered as self-consistent.

The corresponding values of the parameters for the shear viscosity of water in the temperature interval 315 K < T < 620 K are quoted in Table 2. No additional comments are needed here, because they are the same as for argon.

### 3. Contradiction of Ideas

#### Concerning the Activation Mechanism of Molecular Motion

Formula (2) reflects the application of quasicrystalline approach to the description of a thermal motion of molecules in liquids [4]. In this scenario, the molecules fluctuate near their temporary equilibrium positions during a certain characteristic time \( \tau_0 \). Afterward, they jump to a new temporary equilibrium position. It is assumed that the jump-like transition requires that a molecule should overcome a certain energy barrier, so that the corresponding ki-
netic coefficients become proportional to the factor \( \exp(E_a/k_B T) \). If the characteristic time \( \tau_1 \) of those transitions is substantially shorter than \( \tau_0 \), then this approach is correct.

The transfer processes in such liquids are described by the activation theory [4, 5]. A quantitative agreement with experimental data is achieved by introducing the temperature dependences for the parameters \( \eta_1 \) and \( \eta_2 \), as well as \( E_{a1} \) and \( E_{a2} \). As a result, the agreement with experimentally observed viscosity values is obtained for ionic liquids and liquids that can transit into the vitreous state [6–8]. However, unfortunately, the discussion of the physical meaning of introduced parameters is often omitted.

3.1. Shear viscosity

The behavior of the shear viscosity in liquid argon on the coexistence curve, as well as on isochores and isobars, has been studied in detail in work [26]. Here are the arguments that demonstrate an evident discrepancy between the specific features in the temperature dependence of the shear viscosity of argon with the picture of the quasicrystalline character of the molecular thermal motion. Really, the isochoric viscosity values correspond to the magnitude of the dimensionless activation energy \( E_a/k_B T_c \), which is much lower than 1. In other words, the activation energy does not exceed the thermal noise energy, \( E_a < k_B T_c \), which is senseless. Moreover, the activation energy values turn out negative on many isochors. At the same time, the activation energy values on the isobars and the coexistence curve differ considerably from those on isochors (Table 3).

Let us supplement these qualitative considerations with the quantitative analysis of the relation among activation energy values for various mechanisms. Let us proceed from the following expression for the kinematic shear viscosity on isochores:

\[
\nu = \nu_0 \exp(\varepsilon_a(n)/T),
\]

where \( \varepsilon_a(n) = E_a(n)/k_B \). When shifting along an isobar, the activation energy value becomes equal to

\[
\varepsilon_{\text{eff}} = \varepsilon_a(n) - T \frac{d\varepsilon_a(n)}{dn} \frac{dn}{dp} \frac{dT}{dp}.
\]

Substituting the numerical values of corresponding derivatives into this formula, we obtain \( \varepsilon_{\text{eff}} = 1.19 \), which is in total agreement with the data in Table 3. Hence, the effective activation energies for the shear viscosity and self-diffusion considerably depend on the direction of the system state change. In order to determine the corresponding isochoric values, a relevant recalculation has to be done. This circumstance was also marked in work [24]. The \( E_a/k_B T_c \)-values on argon isochors clearly evidence

<table>
<thead>
<tr>
<th>( \xi = 1/5 )</th>
<th>( \xi = 1/4 )</th>
<th>( \xi = 1/3 )</th>
<th>( \xi = 1/2 )</th>
<th>( \xi = 2/3 )</th>
<th>( \xi = 3/4 )</th>
<th>( \xi = 4/5 )</th>
<th>( \xi = 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 - R^2_\xi )</td>
<td>0.775</td>
<td>0.937</td>
<td>0.986</td>
<td>0.974</td>
<td>0.885</td>
<td>0.821</td>
<td>0.782</td>
</tr>
<tr>
<td>( \tilde{\nu}_0 )</td>
<td>1.0001072</td>
<td>1.000009</td>
<td>0.99988</td>
<td>0.99795</td>
<td>0.98994</td>
<td>0.98373</td>
<td>0.97927</td>
</tr>
<tr>
<td>( \zeta^{1/\xi} )</td>
<td>9.63028E-06</td>
<td>3.159E-05</td>
<td>0.00017</td>
<td>0.00162</td>
<td>0.00586</td>
<td>0.00927</td>
<td>0.01173</td>
</tr>
<tr>
<td>1 - ( \tilde{\nu}_0 )</td>
<td>-1.0718E-05</td>
<td>-8.965E-06</td>
<td>0.00012</td>
<td>0.00241</td>
<td>0.01006</td>
<td>0.01628</td>
<td>0.02073</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \rho = \text{const} )</th>
<th>( p = \text{const} )</th>
<th>Coexistence curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho/\rho_c )</td>
<td>( P/P_c )</td>
<td>( E_a/k_B T_c )</td>
</tr>
<tr>
<td>1.12</td>
<td>5.14</td>
<td>1.37</td>
</tr>
<tr>
<td>1.34</td>
<td>10.28</td>
<td>1.25</td>
</tr>
<tr>
<td>1.49</td>
<td>15.42</td>
<td>1.17</td>
</tr>
<tr>
<td>1.87</td>
<td>20.56</td>
<td>1.19</td>
</tr>
<tr>
<td>2.24</td>
<td>0.012</td>
<td>2.61</td>
</tr>
</tbody>
</table>
that the character of the thermal motion of argon molecules differs drastically from the quasicrystalline one.

3.2. Voids in the molecular system

A substantial difference between the values of the self-diffusion coefficients in liquids near their triple points and in the neighborhood of crystalline states (see work [27]) is often explained by the existence of voids in the liquid structure. The fallacy of such notions follows directly from the temperature dependence of the function \( f(t) = \delta/\sigma \), where \( \delta = \langle r_{12} \rangle - \sigma \) is the average value of the gap between the nearest molecules (ions), \( \langle r_{12} \rangle \) the mean distance between the particles, and \( \sigma \) the particle diameter. In other words, this function describes the relative size of the gap between the closest neighbor molecules. It is evident that

\[
f(t) = \frac{v^{1/3}(t) - v_0^{1/3}}{v_0^{1/3}}, \tag{5}
\]

where \( v \) is the specific volume per particle, and \( v_0 \) the own particle volume. The latter parameter is very close to the specific volume at the triple point (or the melting point for metals). The temperature dependences \( f(t) \) for water, argon, and some metals are shown in Fig. 2.

From Fig. 2, one can see that near the triple point of argon or water (or the melting point for metals), the relative value of the intermolecular gap does not exceed 1%, which is practically the same value as for the system in the crystalline state. In other words, every molecule or ion is in a “cell” whose parameters are close to those in the solid state. As a result, the simple translational motion of molecules in liquids at finite distances is impossible. At the same time, the values of self-diffusion coefficients in the crystalline and liquid states differ from each other by ten orders of magnitude or more, which is difficult to explain by assuming the fluctuation character of the void formation near the diffusing particle. The natural explanation of the difference between the values of the dimensionless activation energies of the system in the solid and liquid states is based on the liquid fluidity or, in other words, on a much more probable azimuthal motion of neighbor molecules at small angles (see Fig. 3). A similar mechanism of self-diffusion in a liquid was proposed for the first time in work [28]. Jump-like displacements are also possible, but their contribution to the self-diffusion coefficient is expected to be approximately the same as in solids.

4. Similarity Relation

An important feature of the molecular thermal motion in water is the possibility of applying the residence time notion, \( \tau_0 \), to its description. This quantity is required, for example, while analyzing the
thermal neutron screening [29–31]. Since \( \tau_0 \) has the same temperature dependence as \( \tilde{\tau}_d \), we may conclude that this parameter is the lifetime of “established” molecular vibrations. Within this time interval, a certain configuration of hydrogen bonds remains unchanged. It is essential that the break of a bond and the formation of a new bond configuration are also associated with a small displacement of the center of mass of a water molecule, \(|\Delta r| \approx 0.1 \text{ Å} [32]\), i.e. with a certain contribution to the self-diffusion process.

In accordance with the aforesaid, a conclusion can be drawn that the temperature dependences of the kinetic properties of liquid water has to consist of two intervals: (i) \( T < T_H \), where \( T_H \approx 315 \text{ K} \) (this interval includes the normal and supercooled states), and (ii) \( T_H < T < T_c \), i.e. this interval includes almost all other liquid states of water. In the former interval, when the temperature decreases, the character of the thermal motion of water molecules becomes more and more similar to that observed in hexagonal ice. In the latter interval, the molecular thermal motion approaches the argon-like behavior as the temperature grows.

Hence, in the temperature interval \( T_H < T < T_c \), the magnitude and character of the temperature dependence of the self-diffusion coefficient in water are assumed to be similar to those observed in liquid argon:

\[
D_s^{(w)}(T_w) = \frac{\sigma_w}{\sigma_{Ar}} \left( \frac{\varepsilon_w m_{Ar}}{\varepsilon_{Ar} m_w} \right)^{1/2} D_s^{(Ar)}(T_{Ar}),
\]

where \( T_w \) and \( T_{Ar} \) are the temperatures of the corresponding states for water and argon, respectively,

\[
T_w = \frac{\varepsilon_w}{\varepsilon_{Ar}} T_{Ar};
\]

\( \varepsilon_{Ar} \) and \( \sigma_{Ar} \) are the parameters of the Lennard-Jones potential for argon; \( \varepsilon_w \) and \( \sigma_w \) the parameters of the averaged interaction potential for water molecules, which is similar to the Lennard-Jones potential [33–36]; and \( m_{Ar} \) and \( m_w \) are the masses of an argon atom and a water molecule, respectively.

The values of the parameters \( \varepsilon_w \) and \( \sigma_w \) for the potentials that are used most often to describe the properties of water are quoted in Table 4. The indicated values were calculated at temperatures close to room one. It should be noted that both \( \varepsilon_w \) and \( \sigma_w \) are temperature-dependent, but this dependence is significant only in a narrow vicinity of the critical point. In what follows, the temperature dependence of \( \varepsilon_w \) and \( \sigma_w \) is ignored. The calculation results obtained for the self-diffusion coefficient using formula (6) and their comparison with experimental data are exhibited in Fig. 4.

Note that the same relationship must exist for the coefficients of kinematic shear viscosity,

\[
\nu_w(T_w) = \frac{\sigma_w}{\sigma_{Ar}} \left( \frac{\varepsilon_w m_{Ar}}{\varepsilon_{Ar} m_w} \right)^{1/2} \nu_{Ar}(T_{Ar}),
\]

where \( T_H < T < T_c \).

The calculation results obtained for the kinematic shear viscosity using formula (8) and their comparison with experimental data are shown in Fig. 5.

### 5. Discussion of the Results Obtained

The results obtained in this work confirm our main theses that

(i) the viscosity of liquids in the larger part of the liquid state temperature interval is governed by the friction between the molecular layers that move relative to one another;

<table>
<thead>
<tr>
<th>( \varepsilon_w/k_B T_m )</th>
<th>( \sigma_w \text{ Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.05</td>
<td>2.7</td>
</tr>
<tr>
<td>5.66</td>
<td>2.68</td>
</tr>
<tr>
<td>4.05</td>
<td>2.73</td>
</tr>
<tr>
<td>5.07</td>
<td>2.69</td>
</tr>
</tbody>
</table>

Table 4. Parameters \( \varepsilon_w \) and \( \sigma_w \)

of the averaged interaction potential for water molecules, similar to the Lennard-Jones potential
V.M. Makhlaichuk

(ii) argon and water belong to the same class of similarity of their kinetic coefficients at the temperatures $T_H < T < T_c$ ($T_H \approx 315$ K).

This conclusion follows from the consistency of experimental data for the self-diffusion and shear viscosity coefficients in water, which were calculated on the basis of the similarity principle for the corresponding states of water and argon. We would like to emphasize that this similarity is based on the important fact that the behavior of the shear viscosity of water is determined by the averaged interaction potentials between molecules, which were constructed in works [33–35]. Those potentials are also responsible for the behavior of the specific volume and evaporation heat of water [19].

Not less important is the conclusion about the non-adaptive character of activation mechanisms for the formation of the viscosity and self-diffusion processes in liquids. In the case of rare argon, this fact is considered to be quite convincing [13,24,26]. At the same time, the applicability of the similarity principle stimulates us to conclude that the activation mechanism has no grounds to be applicable in both water and most low molecular fluids. A further analysis of this issue will be carried out separately.

To summarize, I would like to thank Academician Leonid Bulavin for a permanent support of our works concerning the viscosity and self-diffusion in liquids, as well as for the discussion of those issues at the seminars of the Chair of Molecular Physics at the Kyiv National University. I am also sincerely grateful to Prof. M.P. Malomuzh for his consultation and support.

---


Received 02.10.18.
Translated from Ukrainian by O.I. Voitenko

В.М. Махлаичук
ЯКІСНІ ВЛАСТИВОСТІ ЗСУВНОЇ В’ЯЗКОСТІ РІДІН
Р е з ю м е
У роботі наведено обґрунтування того, що 1) в’язкість рідин в більшій частині температурних інтервалів існування їх рідких станів визначається ефектами тертя між молекулярними шарами, що рухаються відносно один одного; 2) аргон і вода при температурах \( T_H < T < T_c \) (\( T_H \approx 315 \) К) належать до одного і того самого класу подібності їх кинетичних коефіцієнтів. За допомогою принципу подібності для відповідних станів води і аргона розраховані коефіцієнти само- і зсувної в’язкості води. В основі цієї подібності лежить той факт, що поведінка зсувної в’язкості води визначається усередненими потенціалами міжмолекулярної взаємодії. В роботі обговорюється неадекватність активаційних механізмів формування процесів в’язкості та самофізії як у воді, так і в більшості низькомолекулярних рідин.