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The effects of hydrogen bonding on the shear viscosity of liquid water

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\textbf{Abstract:} As one of the fundamental physical properties of fluids, viscosity is considered to be the result of intermolecular forces and molecular momentum exchange. In this paper, we assume that hydrogen bonds, as the dominant intermolecular force, dominate the shear viscosity of liquid water and a relationship between the shear viscosity and hydrogen bonding is developed using dimensional analysis, which is further validated by computational chemistry methods. Water, \textsuperscript{*}Electronic mail: nik13@mails.tsinghua.edu.cn
methanol and ethanol are taken as examples to illustrate shear viscosity accounting for intermolecular forces and momentum exchange and their temperature dependence as a result of molecular thermal motions. The calculated shear viscosity of water is consistent with experimental data, which supports the idea that we can use the conceptual model to reveal the nature of shear viscosity.

**Key words:** Viscosity; Hydrogen bonding; Liquid water; Dimensional analysis

1. **Introduction**

   As the most ubiquitous fluid on this planet, liquid water plays a vital role in chemical and biological reactions, as well as in the transmission processes of mass and energy (Ball, 2008; Ludwig, 2001; Turner & Millward, 2002). Shear viscosity, an important physical property of fluids, reflects the ability of resisting shear deformation which is generally considered to be the result of intermolecular forces and the momentum exchange at the molecular level (Vennard & Street, 1982). Viscosity can affect dissolution or dispersion in water (Song & Dai, 2010), and the calculation of shear viscosity based on a realistic water model can provide valuable information on intermolecular forces (Medina et al., 2011).

   Extensive experimental data of shear viscosity of different liquids is available, which can be used to empirically determine the dependence of shear viscosity on temperature and pressure. However, the empirical models are not adequate to reveal
the nature of shear viscosity and some of the empirical parameters in the models may not be related to the intrinsic properties of liquids. A variety of theoretical and computational models have been employed to better understand the liquid viscosity of water.

Theories based on energies and structures of liquids have been developed to illustrate the dependence of shear viscosity on temperature and pressure. De Guzman (1913) and Arrhenius (1917) found that the relationship between shear viscosity and temperature is an Arrhenius type, and Eyring (1936) explained the nature of shear viscosity in a manner analogous to chemical reactions. Considering statistical mechanics and molecular collisions, Castellan (1983) proposed that the propagation of momentum perpendicular to the bulk flow direction is related to the motion of molecules in a single layer in the flow direction. He took into account the mean free path and the mean velocity of molecules. Yang (1992) incorporated the effects of temperature into the mean free path of molecules, to derive an Arrhenius model for the shear viscosity of a liquid. The calculated energy $\Delta E$ was much smaller than the activation energy of hydrogen bonds.

Another way to investigate shear viscosity is to relate it to other transport coefficients. The Stokes-Einstein (Einstein, 1956; Stokes, 1901) equation developed a relationship between shear viscosity and diffusion coefficient, and Debye (1929) developed the relationship between shear viscosity and molecular relaxation time, \( \eta = \left( \frac{kT}{v_m} \right) \tau \) where \( \eta \) is shear viscosity, \( k \) is the Boltzmann constants, \( T \) is
temperature, $v_m$ is the volume of molecules of the solvent, and $\tau$ is the relaxation time. Although the equation is simple in form, the equation is strictly applicable only to Brownian particles, not for molecules. Roland et al. (2006) further developed this method and found the temperature and volume dependence of the relaxation ($\tau(T,V) = \tau(TV^\gamma)$). The magnitude of the coefficient $\gamma$ depends on the strength of the intermolecular forces, although the model is not dimensionally consistent. Eu (2006) took into account two parts for the contribution of shear viscosity, a kinetic part and a potential part. He used the Stokes-Einstein formula and density fluctuation theory to describe the kinetic part and the potential part, respectively. The results for the density and temperature dependence of shear viscosity agreed well with experimental data. In his method, he used some semi-empirical parameters for different liquids and the results for diffusion coefficient at high temperature deviated from the experiment data.

Computational models have also been used to relate the macroscopic properties with microscopic movement through statistical thermodynamics. Potential models, which are built according to information of bond length, bond angle, dipole moment etc. of molecules, are quite important for descriptions of intermolecular forces in molecular simulation. Then the information of shear velocity and position of molecules can be obtained using Newton’s second law. Shear viscosity can be calculated as the integral of the autocorrelation function of velocity according to Einstein’s equation or Green-Kubo’s equation (Allen & Tildesley, 2017; Sadus, 2002).
Shear viscosity calculated using potential energy models for water molecules, e.g. SPC (single point charge), TIP (transferable interaction potential), has normally been found to be smaller than suggested by experimental data value (Ferguson, 1995; Glattli et al., 2002; Mahoney & Jorgensen, 2001; Raabe & Sadus, 2012; Wu et al., 2006), which is shown in Table 1.

Table 1. Shear viscosity of water calculated using different potential energy models

<table>
<thead>
<tr>
<th>Potential model</th>
<th>η(mPas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>0.895</td>
</tr>
<tr>
<td>SPC/E</td>
<td>0.713±0.010</td>
</tr>
<tr>
<td>SPC</td>
<td>0.410±0.010</td>
</tr>
<tr>
<td>TIP3P</td>
<td>0.321</td>
</tr>
<tr>
<td>TIP4P</td>
<td>0.494</td>
</tr>
<tr>
<td>TIP5P</td>
<td>0.699</td>
</tr>
</tbody>
</table>

The properties of some common liquids under standard conditions are shown in Table 2, including the relative molecular mass, density, shear viscosity and existence of hydrogen bonding. When the relative molecular mass or the density of two liquids is similar, the higher shear viscosity associated with hydrogen bonding is apparent. For liquid water, the strength of the hydrogen bonds is an order larger than the van der Waals forces (Israelachvili, 2011). Thus, it is recognized that shear viscosity has a direct and important relationship with the hydrogen bonds, and there is little work
focusing on a quantitative relationship between the two concepts.

Table 2. The relative molecular mass, density, shear viscosity and H-bonding structure of some common liquids

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Relative molecular mass</th>
<th>Density* (kg/m³)</th>
<th>Viscosity* (mPa·s)</th>
<th>H-bonding structure existence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ether</td>
<td>74.10</td>
<td>0.714</td>
<td>0.233</td>
<td>No</td>
</tr>
<tr>
<td>Benzene</td>
<td>78.11</td>
<td>0.879</td>
<td>0.652</td>
<td>No</td>
</tr>
<tr>
<td>Argon</td>
<td>200.59</td>
<td>13.590</td>
<td>1.550</td>
<td>No</td>
</tr>
<tr>
<td>Water</td>
<td>18.02</td>
<td>0.998</td>
<td>1.000</td>
<td>Yes</td>
</tr>
<tr>
<td>Ethanol</td>
<td>46.07</td>
<td>0.789</td>
<td>1.100</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* properties at standard conditions, T=25°C, P=1.013×10⁵ Pa

The hydrogen bonds of water are the electrostatic interactions between dipoles. For a water dimer, the hydrogen bonding is formed when electrons in the lone-pair orbitals on the oxygen atom of one water molecule are donated to the σ_{OH} antibonding orbital situated on the other water molecule (Weinhold & Landis, 2005). Research on hydrogen bonds has been ongoing for many years, and quantum chemistry, thermodynamics and spectroscopy are the major methods for analysis. The two-body and many-body potential energy can be precisely calculated by using quantum chemistry methods (Morawietz et al., 2016; Qian et al., 2010; Santra et al., 2015; Tokmachev et al., 2010), thus providing a good option for the simulation of
larger molecular water systems (Clementi & Corongiu, 2011; Liu et al., 2014). The average number of hydrogen bonds per molecule as well as the relaxation time for hydrogen bonding are slightly different when using different methods to define the hydrogen bonds (Belch & Rice, 1987; Kuo & Mundy, 2004; Medina et al., 2011; Raabe & Sadus, 2012; Wernet et al., 2004). Vibration spectroscopy, including infrared (Rao & Sastry, 1940) and Raman (Rafalowski, 1931), have also been used to probe the structure of hydrogen bonds.

X-ray diffraction measurement provides information on the radial distribution function of oxygen-oxygen atoms (Hura et al., 2000), while neutron diffraction experiments supplement the X-ray diffraction data with information on the radial distribution functions of H-H and H-O atoms (Soper, 2000). Recent efforts to prove behavior under ultrafast conditions (Ashihara et al., 2007; Sellberg et al., 2014) have led to insights into hydrogen-bonding dynamics. Dynamic experiments at ambient conditions show that the formation and transformation of hydrogen bonds occur on timescales of approximately 50 to 100 femtoseconds (Guo et al., 2016; Liu & Wu, 2013).

As hydrogen bonds form and break during the motion of water molecules, the dynamics of the hydrogen bonding dominates the intermolecular forces and influences shear viscosity. There is a need for a better understanding of the effect of hydrogen bonding on the shear viscosity of liquid water. In addition, most of the methods mentioned above all provided descriptions for the microscopic mechanisms of shear
viscosity, but partially neglected the contribution of the momentum exchange of molecular thermal motion (Raabe & Sadus, 2012; Roland et al., 2006; Yang, 1992).

In this paper, we seek to take an alternative view of water viscosity and develop a simple physical model and test that model with ab initio calculations. We assume that the shear viscosity of liquid water is related to the change of hydrogen-bonding structure and the spatial and temporal variation of the structure can be utilized for description of the relationship. Dimensional analysis and quantum chemistry methods are used to develop a quantitative description of the microscopic mechanism of shear viscosity. Then, we take the molecular thermal motion into account and develop a semi-empirical method for describing the temperature dependence of shear viscosity.

2. Methods

2.1 Dimensional analysis

Large numbers of hydrogen bonds form and break when there is relative movement between different fluid layers. There is a thermodynamic equilibrium state given the temperature and pressure, and the energy of the system may slightly fluctuate due to the molecular thermal motion. For a water dimer, both experimental (Dyke & Muenter, 1974) and computational methods (Kollman & Allen, 1969; Morokuma & Pedersen, 1968) show that the distance between nearest oxygen atoms is approximately 3.0 Å in the equilibrium state. According to neutron diffraction
experiments (Djikaev & Ruckenstein, 2011; Gallagher & Sharp, 2003; Henao et al., 2016; Petersen et al., 2013) and computational calculation results (Kuo & Mundy, 2004), at the critical state at which hydrogen bonds come into play, the distance of nearest oxygen atoms is approximately 3.5 Å.

As the distance between water molecules changes frequently, the energy of the hydrogen bonding structure changes. The lifetime of a hydrogen bond is the time during which one hydrogen bond forms and breaks. Therefore, the change process of the hydrogen bonds can be characterized by characteristic energy (denoted as $E$), characteristic volume (denoted as $V$) and the lifetime of the hydrogen bonds (denoted as $t$). Assuming that shear viscosity $\eta$ depends upon the energy $E$, the volume of the water dimer $V$ and the time $t$ satisfy the functional relation that is shown in equation (1):

$$f (\eta, E, V, t) = 0$$

(1)

A dimensionally consistent form of this relationship can be written, as shown in equation (2)

$$F (\frac{\eta}{(E t / V)}) = 0$$

(2)

Thus, for an empirical coefficient, $A$, shear viscosity is described by equation (3)

$$\eta = A (E / V) t$$

(3)

The characteristic energy $E$ is chosen as the energy difference between the equilibrium state and the critical state, and it only depends on configuration instead of temperature. At the critical state, we choose the radial distance of nearest oxygen
atoms as the characteristic length. The equilibrium separation of the molecules defines the characteristic volume $\Delta V$. The lifetime of the hydrogen bonds is chosen as the characteristic time, and it is a function of temperature. The critical state and the equilibrium state are shown in Fig. 1. We draw two tangential circles in the critical state, using the two oxygen atoms as the centers. At the equilibrium state, the two circles approach to each other, and the two circles intersect. $\Delta V$ is defined to be the volume of the intersection and it can be calculated using the hemispherical segment formula, referring to equation (4).

Fig. 1. (a) The spheres in the critical state (b) The spheres in the equilibrium state

$$\Delta V = 2\pi (D_{cr} - D_{eq})^2 \left( \frac{D_{cr}}{3} + \frac{D_{eq}}{6} \right) / 4 \quad (4)$$

Where $D_{cr}$ and $D_{eq}$ are the distance of oxygen-oxygen in critical state and equilibrium state, respectively.

2.2 Regression analysis

According to Arrhenius’ law, for a liquid with relatively large intermolecular forces, the relationship (Arrhenius, 1917) between shear viscosity coefficient and temperature can be described by equation (5)

$$\eta = A \exp \left( \frac{\Delta \varepsilon_{vis}}{RT} \right) \quad (5)$$

This equation shows the effects of intermolecular forces on viscosity, in which $\eta$ represents the viscosity coefficient. $A$ is a constant, and $\Delta \varepsilon_{vis}$ is the activation energy.
For gases, the distance between molecules is great and the intermolecular forces are relatively small. Therefore, the viscosity of a gas fluid is believed to be dominated by molecular thermal motion. The relationship (Arrhenius, 1917) between shear viscosity coefficient and temperature is given by equation (6)

\[ \eta = 2 (MR)^{\frac{1}{2}} T^{\frac{3}{2}} / \left(3\pi^2 N_A \sigma^2\right) \]  

(6)

In this equation, \( \eta \) represents the shear viscosity coefficient. \( M \) is the molar mass, and \( R \) is the ideal gas constant. \( N_A \) represents the Avogadro constant, and \( \sigma \) is the diameter of the molecule.

As has been mentioned previously, the reaction energy that is calculated by regression analysis is not strictly constant, potentially due to the neglect of molecular thermal motions. Instead a model of shear viscosity is developed that combines Equation (5) with the form of Equation (6)

\[ \eta = A \exp\left(\frac{B}{T}\right) + CT^{\frac{1}{2}} \]  

(7)

This form was tested by fitting shear viscosity data of liquid water, methanol and ethanol at different temperatures. The three parameters can be used to analyze the effects of reaction energy, intermolecular forces and molecular thermal motion on shear viscosity.
3 Results and discussion

3.1 The relationship between hydrogen bonding of a water dimer and viscosity

Ab initio calculations were conducted to calculate and analyze the geometry and energy of the equilibrium state and critical state of a water dimer under standard condition, with the purpose of checking the results of the dimensional analysis. The computational calculation was conducted in Gaussian09. We utilized the Hartree-Fock method and 6-311++G** basic sets and then conducted a flexible scan with 0.03 Å as the scanning interval of oxygen-oxygen.

The potential energy as a function of water molecule separation distance is shown in Fig.2. In the equilibrium state, the energies of a water dimer and a water monomer are -152.12 ha and -76.05 ha, respectively. The calculated binding energy of a water dimer is 4.8 kcal/mol, which is close to the experimental result 3.6±0.5 kcal/mol (Curtiss et al., 1979) and simulated result 5.0±0.1 kcal/mol(Feyereisen et al., 1996).

At the critical state, the distance of nearest oxygen atoms is 3.5 Å, the energy of a water dimer is -152.11276 ha, and the angle between the O-H bond of the donor and the angular bisector of the H-O-H of the acceptor is 34 degrees, which is similar to the results of the molecular simulations (Kuo & Mundy, 2004).
In the liquid state, the combination \( \frac{\Delta E}{\Delta V} \Delta t \) is \( 1.12 \times 10^{-3} \text{Pa} \cdot \text{s} \), which is similar in magnitude to the measured shear viscosity at ambient condition\( 0.89 \times 10^{-3} \text{Pa} \cdot \text{s} \), that is effectively A in Equation (3) is 0.794).

It is intuitive that as the temperature increases, the thermal motion of water molecules become more likely to influence the potential of the system. The fluctuation of the system at higher temperature shortens the relaxation process of hydrogen bonding, and the lifetime of the hydrogen bonds becomes shorter. We presume the lifetime of hydrogen bonds to evolve as the temperature changes with an exponential relation with the coefficient of \( 1/T \), while the energy and the volume remain constant. The temperature dependence of shear viscosity is also shown in Fig.3.

Fig.3. The temperature dependence of viscosity and lifetime of hydrogen bonds

The results show that the lifetime of the hydrogen bonds are consistent with experimental and molecular simulation results at low temperature (273K~293K), while at higher temperature up to 373K, the calculated lifetime of the hydrogen bonds is about 1/4 of the experimental and molecular simulation results (Guo et al., 2016; Liu & Wu, 2013) due to neglect of the molecular thermal motion.
3.2 The contribution of the molecular force and the molecular thermal motion to shear viscosity

Water, methanol and ethanol were chosen as example liquids to illustrate the contribution of the molecular force and the molecular thermal motion to shear viscosity. The use of Equation (7) to correlate shear viscosity is shown in Fig.4. The values of the constants in Equation (7) are listed in Table 3.

![Shear viscosity of three liquids: water, methanol and ethanol and comparison to Equation (3)](image)

The resulting reaction energies of water, methanol and ethanol in Equation (7) are 20.7, 11.7 and 13.4 kJ/mol (Vargas-Caamal et al., 2015), respectively. The energy of liquid water is almost as great as the hydrogen bonding energy (21 kJ/mol). The reaction energy of methanol is 4 kJ/mol smaller than the hydrogen bonding energy (15 kJ/mol). There are two types of hydrogen bonding structures in ethanol. The first molecular geometry construction is dictated by intermolecular O-H…O hydrogen bonds where a hydroxyl hydrogen interacts with an oxygen atom. The other molecular geometry construction is dictated by C-H…O hydrogen bonds where an alkyl hydrogen interacts with an oxygen atom. The binding energies of the two geometries are 22.9~30.1 kJ/mol and 8.4~14.3 kJ/mol, respectively. Therefore, the energy calculated by the fitting results of ethanol shows that the C-H…O hydrogen bonds might dominate the hydrogen bonding structure in ethanol.
Table 3. The fitting constants of the three liquids: water, methanol and ethanol

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (10^6\text{Pa} \cdot \text{s})</td>
</tr>
<tr>
<td>Water</td>
<td>0.18</td>
</tr>
<tr>
<td>Methanol</td>
<td>4.16</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4.76</td>
</tr>
</tbody>
</table>

In equation (6), the coefficient of \(T^{1/2}\) is \(2(MR)^{1/2}/3\pi^{3/2}N_A\sigma^2\), denoted as \(C_0\). The results of the parameters of the three liquids are shown in Table 4 (Patnaik, 2004).

Table 4. The parameters of the three liquids

<table>
<thead>
<tr>
<th>Liquid</th>
<th>M (kg/mol)</th>
<th>(\sigma) ((\text{Å}))</th>
<th>(C_0)</th>
<th>(C/C_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.018</td>
<td>2.76</td>
<td>1.01</td>
<td>7.9</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.032</td>
<td>4.40</td>
<td>0.53</td>
<td>9.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.046</td>
<td>4.70</td>
<td>0.56</td>
<td>2.2</td>
</tr>
</tbody>
</table>

In liquid phase, the small distance between molecules increases the probability of collision and the frequency of momentum transfer, thus resulting in the shear viscosity calculated via equation (6) being one order smaller than the second component of the fitting shear viscosity, i.e. \(CT^{1/2}\). It can be concluded that the contribution to shear viscosity from momentum transfer in liquid phase is much larger than predictions by
equation (6) as would be expected. The contribution of intermolecular forces and molecular thermal motion is shown in Fig.5. At low temperatures from 273 K to approximately 310 K, the intermolecular forces dominate the viscous effects, with more than 80% of the total shear viscosity value. As the temperature increases to the boiling point, the momentum transfer due to molecular thermal motion make an increasingly important contribution to shear viscosity.

Fig.5. The contribution of the two components of shear viscosity as the temperature changes

4 Conclusions

We used dimensional analysis to identify the form of the relationship between shear viscosity and the hydrogen bonding energy and bond relaxation time. We calculate the change in volume and energy of a water dimer between the critical and equilibrium state to relate to shear viscosity. Furthermore, we relate the shear viscosity change under different temperatures to the lifetime of the hydrogen bonds. By considering the molecular thermal motions in liquid phase, we discuss on the contributions of the intermolecular forces and molecular thermal motions to shear viscosity under different temperatures, which may give a reasonable explanation for the deviation of the previous results from experimental data under high temperature.

In the macroscopic view, the vertical gradient of the velocity reflects the relative motion between different water layers. The velocity gradients causes the breakage and
formation of hydrogen bonds in the femtosecond time scale. In the hydrogen bonding structure, as the distinction grows, the water dimer evolves from the equilibrium state to the critical state, and the bonds then break, reducing shear viscosity.

Acknowledgements

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