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Correlation of Translational and Rotational Motion of Water Molecules in Molecular Dynamic Models

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Abstract: The motion of a rigid molecule in a computer model can be described as the sum of the displacement of the center of mass of the molecule and the rotation of the molecule around an axis passing through this center. The interaction of a molecule with its environment leads to a correlation between these movements. Earlier in [1], we studied the distributions of angles between the directions of the displacement vectors and the axes of rotation of water molecules, as well as between them and the internal vectors of these molecules. This paper describes the correlation of the magnitudes of these displacements, that is, the lengths of the displacement vectors and angles of accompanying rotations. The correlation coefficients of these characteristics are calculated for intervals of different durations at different temperatures and pressures, and the characteristic times of preservation of these correlations are determined. We believe that the times found by us represent the lifetimes of the local environments of molecules. For water molecules, a change in the local environment is accompanied by a change in the structure of the nearest section of the network of hydrogen bonds, and therefore the lifetimes of local environments are close to the lifetimes of these bonds.

Keywords: molecular dynamics simulation, water, translational displacement, angular displacement, correlation of displacement and rotation

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1. INTRODUCTION

The movement of any molecule can be decomposed into two formally independent movements - translational and rotational. The movement of the center of mass of the molecule can be considered as a translational one. Then the remaining motion will represent the rotation of the molecule around an axis passing through this center. If the molecule is rigid, that is, the changes in the distances between its atoms are negligible, such a description will

unambiguously predict the position and motion of each atom in the molecule.

The result of molecular dynamics modeling is a set of coordinates of the centers of all atoms in the model relative to the initially specified coordinate system. The radius vector connecting the origin of the coordinate system with the center of the atom describes the position of that atom. The vector connecting the position of the center of the atom at the beginning and at the end of a certain time interval describes the movement of the atom in this interval. That is, both the position and the movement of the atom are described in the same form - in the form of a vector.

We propose to reduce the description of molecular rotation to an equally simple scheme. To do this, we define our own coordinate system for each type of molecule. We place the origin of this coordinate system at the center of mass of the molecule, and choose the direction of the axes according to the position of its atoms. The orientation of the molecule in which the directions of the axes of its own system coincide with the directions of the axes of the coordinate system of the model box will be called the basic or zero orientation. Any current orientation can be unambiguously described by the parameters of rotation that transfers the molecule from the basic orientation to the current one. Thus, we will define the space of orientations of the selected type of molecules, in which the role of the origin will be played by the basic orientation of these molecules, and the parameters of rotation, which translates it into the current orientations, will be used as the coordinates of these orientations. Rotation that transfers the molecule between two orientations will be accompanied by a change in coordinates in this space, and therefore represent a movement in it. That is, with this approach, both the current orientations and rotations between them will be recorded using the rotation parameters.

This approach can be implemented using any method of describing rotations, for

example, using Euler angles or rotation matrices. However, the quaternion algebra turned out to be the most convenient for this. A quaternion is a hypercomplex number with one real and three different imaginary components. Each rotation by an angle φ around the unit axis \mathbf{u} corresponds to a quaternion, the real part of which is equal to $\cos(\varphi/2)$, and the three imaginary ones correspond to the vector $\mathbf{u} \cdot \sin(\varphi/2)$ directed along the rotation axis. That is, unlike other ways of describing rotation, the quaternion contains rotation parameters almost explicitly. The Appendix in [1] provides a detailed description of the procedures for using the algebra of quaternions to describe the current orientations, rotations between them and the transformation of vectors in the transition from the internal coordinate system of the molecule to the coordinate system of the model and vice versa.

The translational and rotational motions are independent only for an isolated molecule. The interaction of the molecule with the environment leads to a correlation between these types of movements. In [1], we showed that in the model of liquid water most often the displacement vector is perpendicular to the axis of rotation. At the same time, the displacement vector is often parallel to the normal vector, and the rotation axis is parallel to the line passing through the centers of the hydrogen atoms of this molecule. These patterns correspond to motion in which a water molecule sways on the two strongest hydrogen bonds, usually those in which this molecule participates as a proton donor. However, all distributions are wide enough, and therefore the presented picture describes only the most probable types of motion of water molecules, and does not cover all their diversity. In this work, we study the correlations of not directions, but the magnitudes of spatial displacements and angles of rotation of molecules, and also determine the characteristic times of conservation of these correlations.

2. MODELS

We used water models prepared using the LAMMPS molecular dynamics simulation package [2]. Each model contains 8000 molecules with the TIP4P/2005 potential [3] in a cubic box with periodic boundary conditions, the simulation time step is 2 fs. The following thermodynamic conditions were realized in the models: temperatures of 260, 280, 300, 330 and 360 K at a pressure of 1 bar, as well as pressures of 2, 5, 10 and 15 Kbar at a temperature of 300K. The preliminary relaxation lasted for at least 1 ns. The analysis of displacements and rotations was carried out using 20,000 instant configurations every 200 fs. For each molecule of these configurations, the coordinates of the centers of mass of the molecules were determined, as well as the quaternions of their current orientations [1]. The translational and angular displacements were calculated for time intervals of 0.2, 0.4, 0.6, 1, 2, 4, and 6 ps. The results for each interval were averaged over approximately 20,000 pairs of start and end configurations.

The autocorrelation functions of the velocities and lifetimes of hydrogen bonds were calculated based on other sets of configurations of the same models. Each set contained 60,000 snap shots at each simulation step every 2 fs.

3. TRANSLATIONAL AND ANGULAR DISPLACEMENTS

Let us first consider the translational and rotational displacements separately. **Fig. 1** shows the distributions of translational (a) and rotational (b) displacements of water molecules for different time intervals in the model at a temperature of 300 K and a pressure of 1 bar. The insets show the dependence of the mean squares of the corresponding displacements on the duration of the movement. This dependence for translational displacements after 1 ps looks like a straight line in accordance with Einstein's formula for three-dimensional space. Rotational displacements can be considered as displacements on the surface of a sphere. In the model of random independent (Brownian) rotations at small angles of complete rotation, where the surface of the sphere is practically flat (the cosine of the angle is very close to 1), the mean square of the angle of rotation is also proportional to time according to Einstein's formula for random motion on a plane. However, even in such a model, as the angle increases, the slope of the dependence gradually decreases, first due to the increasing deviation from the plane, and then due to the limitation of the reliably determined angle of rotation to the value π . In the water model,

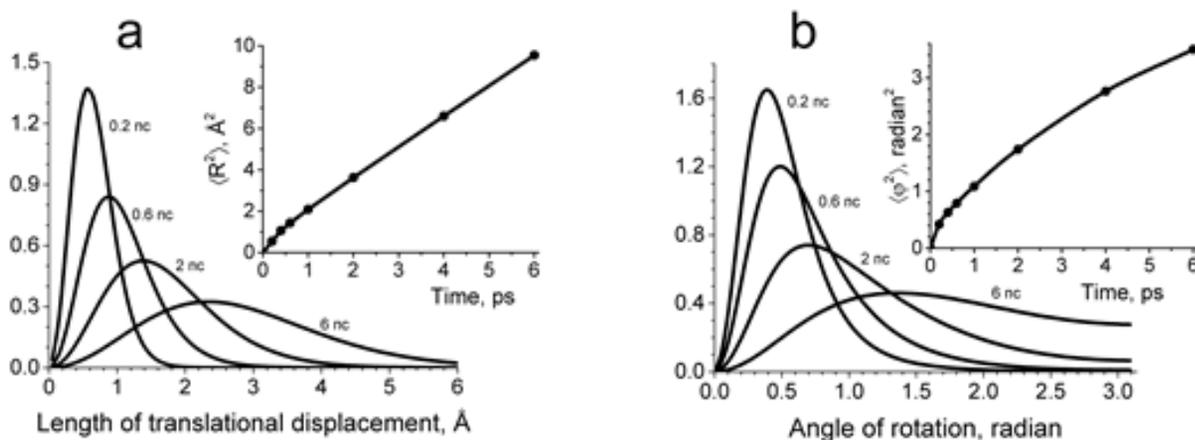


Fig. 1. Distributions of translational (a) and angular (b) displacements of water molecules at $P = 1$ bar, $T = 300K$ for different time intervals (indicated near the curves). The insets show the time dependences of the mean squares of the corresponding displacements.

there is a correlation between successive steps in molecular dynamics. Therefore, the dependence of the mean square of the rotation angle deviates from a straight line even for short times, just as it manifests itself in the time dependence of the mean square of the length of the translational displacement of the center of mass. As a result, a straight line nowhere describes the dependence of the mean square of the rotation angle in the water model (Fig. 1b).

The correlation between the velocities of molecules in successive steps of the simulation can be shown using an autocorrelation function. To calculate this function, we used as the initial 50,000 configurations from the set of configurations in 2 fs, and calculated the average dot products of the velocities in the initial and sequential configurations. For the translational motion, the velocities of oxygen atoms were used, and the angular velocities were extracted from the quaternions of rotation, calculated by comparing the quaternions of the orientations of the molecules in the initial and final configurations.

Fig. 2 shows the autocorrelation functions of the translational (dotted line)

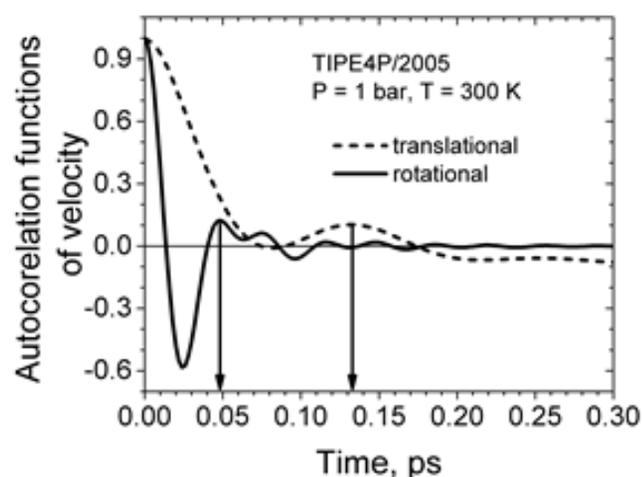


Fig. 2. Normalized autocorrelation functions of translational and rotational velocities of water molecules at $P = 1$ bar and $T = 300$ K. Arrows show the positions of the second maxima corresponding to the periods of the main translational and librational oscillations.

and rotational (solid line) velocities of water molecules, normalized to the mean square of the corresponding velocities. The normalized autocorrelation functions start with a value of 1 (ideal correlation of the initial velocities with themselves) and initially decrease monotonically, since the moduli and directions of the molecular velocities gradually change over time. The position of the first minimum marks the time at which the largest number of molecules reversed their velocities. The second maximum represents the time at which the largest number of molecules was again moving in the original direction. The positions of these maxima correspond to the periods of the main fluctuations. The period of translational oscillations is approximately 130 fs (from 117.1 fs in the model with the highest pressure to 134.8 fs in the model with the highest temperature), the libration period is approximately 47 fs (from 45.3 fs to 49.3 fs in the same models). This means that during one translational vibration, a water molecule performs several librational vibrations. The complex form of the autocorrelation function of angular velocities suggests that a water molecule participates simultaneously in several librational vibrations with close frequencies.

4. CORRELATION OF TRANSLATIVE AND ANGULAR DISPLACEMENTS

The correlation between the modules of translational and rotational displacements can be depicted using the two-dimensional diagram shown in Fig. 3. Here we used the displacements of water molecules for the 0.6 ps interval in the same model as in the previous figures. This diagram shows that the correlation between these modules is clearly present, and it is positive, although rather weak.

The correlation between arbitrary characteristics x and y of the same system of n

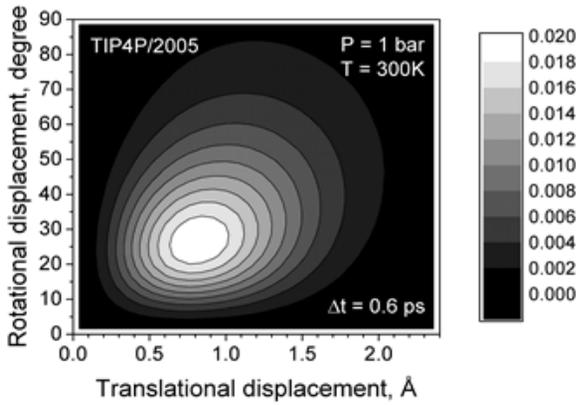


Fig. 3. Joint distribution of the length of displacements of the center of mass of the water molecule (horizontally) and the angle of its rotation (vertically) during the movement of 0.6 ps.

objects can be numerically described using the Pearson correlation coefficient:

$$r_{xy} = \frac{\sum_{i=1}^n (x_i - \langle x \rangle) \cdot (y_i - \langle y \rangle)}{\sqrt{\sum_{i=1}^n (x_i - \langle x \rangle)^2 \cdot \sum_{i=1}^n (y_i - \langle y \rangle)^2}}, \quad (1)$$

where $\langle x \rangle = (\sum_{i=1}^n x_i) / n$ is the average value of the characteristic x . The error in calculating this coefficient is determined by the formula

$$m_{xy} = \sqrt{(1 - r_{xy}^2) / (n - 2)}.$$

We used an identical, but more convenient formula:

$$r_{xy} = \frac{\langle xy \rangle - \langle x \rangle \cdot \langle y \rangle}{\sigma_x \cdot \sigma_y}, \quad (2)$$

where $\langle xy \rangle = (\sum_{i=1}^n x_i \cdot y_i) / n$, $\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$, $\langle x^2 \rangle = (\sum_{i=1}^n x_i^2) / n$. The correlation coefficient changes from maximum +1 (ideal correlation, when characteristics increase and decrease simultaneously and equally) to minimum -1 (ideal anticorrelation, when an increase in one characteristic is accompanied by a synchronous decrease in another characteristic). For completely independent characteristics, the coefficient is 0. The correlation coefficient of the displacements shown in Fig. 3 is $r_{xy} = 0.303$, and the error in its determination is $m_{xy} = 0.00024$. This means that there is a weak positive correlation between the values of translational and rotational displacements in this model.

The value of the correlation coefficient of translational and rotational displacements of water molecules depends on the thermodynamic conditions of the model, as well as on the duration of motion Δt . The results are presented in **Fig. 4** for models with different temperatures (a), and with different pressures (b). An increase in temperature or pressure for any fixed duration of movement decreases the value of the correlation coefficient.

The dependence of the correlation coefficients on the duration of movement under any thermodynamic conditions passes through a maximum. The position of this maximum strongly depends on temperature (from 0.5 to

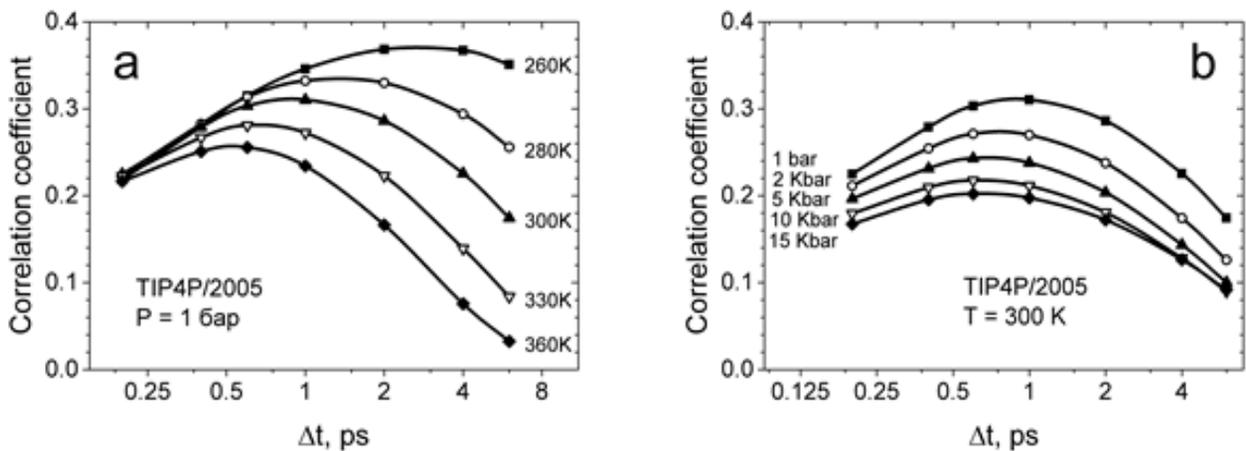


Fig. 4. Dependence of the correlation coefficient of translational and rotational displacements on the duration of motion Δt for models with different temperatures (a) and pressures (b).

2.7 ps) and is almost independent of pressure (from 0.6 to 0.9 ps) (see also Fig. 5). These times are much longer than the periods of translational oscillations (of the order of 130 fs) and the more so of librational oscillations (of the order of 50 fs), which were determined by us from the autocorrelation functions of velocities.

Thus, the correlation between translational and rotational displacements is preserved, although the water molecule at this time performs many translational and librational vibrations. This means that all these vibrations take place in an unchanging local environment. The growth of the correlation coefficient at small times is associated with the leveling of random deviations of the current shape of the local environment from its average equilibrium shape. A decrease in the coefficient at large times is due to an increase in the number of molecules whose local environment has changed. As a result, more and more often, the initial and final positions of the molecule are trapped inside different local environments, in which the movements do not correlate in any way. The duration of the time interval at which the correlation of translational and rotational motion is manifested to the greatest extent can be taken as the characteristic time of preservation of the initial local environment of water

molecules in an almost unchanged form, that is, the lifetime of this local environment.

5. LIFE TIME OF HYDROGEN BONDS

A water molecule is hydrogen bonded with many molecules of its local environment. The change in the shape of the local environment usually occurs when some of the old hydrogen bonds are broken and a few new ones are formed. Fig. 5 compares the lifetimes of local environments Δt_{\max} and the average lifetimes of hydrogen bonds, calculated according to two different criteria. As before, Fig. 5a contains dependences on temperature, and Fig. 5b on pressure. The lifetimes of local environments Δt_{\max} are shown by black squares. The empty circles represent the lifetimes of hydrogen bonds, determined according to a simple geometric criterion often used to calculate them. According to this criterion, a bond between molecules exists if the distance between the centers of their oxygen is $R_{\text{OO}} < 3.3 \text{ \AA}$, and the minimum distance between the oxygen of one molecule and one of the hydrogen of the other is $R_{\text{OH}} < 2.45 \text{ \AA}$.

Earlier in works [4-5], we noted that in this case a lot of bonds arise, which are restored after a short-term rupture. Since the restoration of the hydrogen bond means that the given pair of molecules remained close to each other, we considered that the shortest breaks could be

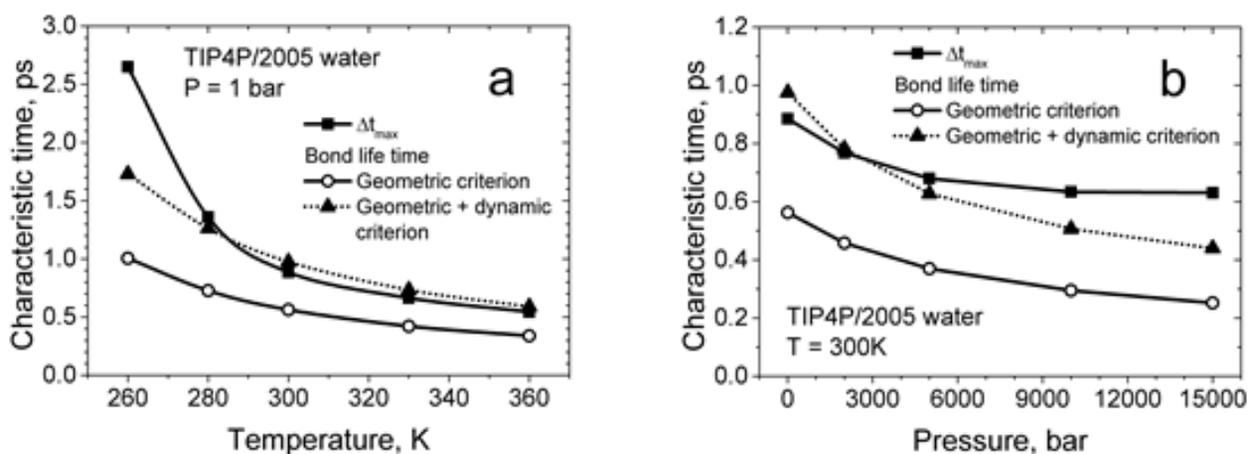


Fig. 5. Comparison of the characteristic lifetimes of local environments of water molecules Δt_{\max} (■) with the average lifetimes of hydrogen bonds, determined by a purely geometric criterion (○), as well as by a combined geometric-dynamic criterion. (▲).

ignored. Therefore, in the second criterion, we added a dynamic one to the geometric part, according to which the bonds were considered broken only if the duration of the break exceeded half the period of the main translational oscillations. We determined the period of translational oscillations by the position of the second maximum of the autocorrelation function of velocity, as it was done in Fig. 4. The duration of the ignored break in different models ranged from 58 to 68 fs. The bond lifetimes determined according to this combined criterion are shown in Fig. 5 by triangles.

According to the geometric criterion, the lifetimes turned out to be 1.5-2 times shorter than the lifetimes of the local environment. However, the lifetimes according to the combined criterion correspond to this time much better. The largest deviations are observed at the lowest temperature (260 K) and at high pressure (from 5 Kbar and above). Perhaps these deviations are due to the fact that in these models, according to the combined criterion, water molecules have the largest average number of hydrogen bonds (almost 4 at $T = 360$ K and about 4.5 at $P = 15$ Kbar). So, to change the local environment, it is required to break more bonds at the same time, since otherwise the previously broken bond can be restored and prolong the existence of the current environment.

6. CONCLUSION

The interaction of water molecules with its environment leads to a correlation between translational and rotational motion. The Pearson correlation coefficient between the length of the translational displacement of the water molecule and the angle of its rotation during the same time does not exceed 0.4, which means the presence of a weak positive correlation between these characteristics. An increase in temperature and pressure leads to a decrease in the coefficient. However, its value also depends on the duration of the movement. An increase in the duration

of movement in each model is first accompanied by an increase in the coefficient, and then by its monotonic decrease. We suppose that a decrease in correlation occurs after a change in the local environment of the molecule, and therefore we propose to consider the time of motion at which the coefficient reaches its maximum value as the average lifetime of local environments. This time significantly exceeds the periods of the main translational and librational oscillations, which means that during the lifetime of the local environment of the molecule, it manages to perform many such oscillations.

According to the theory of thermal motion of molecules in a liquid, proposed by Ya.I. Frenkel, each liquid molecule vibrates for a noticeable part of the time inside the "cell" formed by the molecules of the local environment. The exit from the cell occurs only after its destruction. Perhaps the time we found is the time of the settled life of a water molecule, and we have implemented a method to determine it. In [6], it was suggested that it is the presence of hydrogen bonds that leads to such a significant difference in the behavior of a water molecule during sedentary life inside a cell and during transitions between cells. Therefore, it is not surprising that the lifetime of the local environment in water found by us is close to the lifetime of hydrogen bonds in it. Moreover, these times show practically the same dependences on temperature and pressure.

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