

COMPUTER INVESTIGATION OF PHYSICAL PROPERTIES OF WATER CLUSTERS.

1. STABILITY

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The method of molecular dynamics is applied to investigate the stability of water clusters containing up to 90 molecules. With increasing size of aggregates, $(\text{H}_2\text{O})_{n \geq 10}$, their thermal stability strengthens. Mechanical stability of great clusters keeps the quickly reached level, and the coefficient of dielectric stability passes through the maximum at $n = 50$.

Keywords: water, dipole moment, dielectric constant, isodynamic criteria of stability, cluster, molecular dynamics, compressibility, heat capacity.

INTRODUCTION

By virtue of exclusive biological importance, water and aqueous media became a subject of steadfast research, in particular by the methods of computer modeling. The majority of structural and dynamic properties of bulk water are investigated using pair interaction potentials [1-3]. However, recently the models of water [4, 5] considering many-body interactions have been created. On this basis, the evolution of distortion of tetrahedrality of water structure is investigated, and characteristics of reorientation of water molecules [6] are found. Also it has been shown that three-body interactions influence the mean force field formed around the water molecule, including a little change in the character of movement of the neighboring molecules forming a cell, where the molecule vibrates and rotates. In parallel to standard MD simulations, the *ab initio* molecular dynamics method has been developed [7].

The basic disadvantage of the methods using three-body interaction potentials or *ab initio* methods is the essential increase in computer expenses and, as a consequence, the reduction of length of calculations. In molecular dynamics methods considering properties of the water clusters whose size comes to 100 molecules, it is expedient to use traditional techniques in order to provide the duration of calculations not less than the period of vibrations of molecules in virtual cells, t_{vib} . The time t_{vib} is commensurable with an average time of reorientation of polar molecules, t_{reor} . NMR experiments show that the reorientation time of dipoles in water, t_{reor} , is approximately 4.8 ps at 293 K [8], and the theoretical value of a dielectric relaxation time equals $t_{\text{D}} = 8.5$ ps [9].

Movements of molecules are more correlated in water clusters than in rarefied water vapor. At the same time, the nature of molecule movements in clusters differs from their typical moving in bulk water. For example, mean square displacement of the molecule centers in radial and tangential directions of a spherical cluster differs. The character of dynamics of molecules affects the stability and structure of the water aggregate.

The purpose of the present work is to investigate the influence of the aggregate size on the cluster stability and to

estimate the reliability of various criteria of stability with reference to systems with the limited number of degrees of freedom.

COMPUTER MODEL

Intermolecular interaction in a system is described on the basis of the advanced four-centre potential for water molecules [11] and with allowing for polarization of water molecules. The geometry of a monomer in this model is constructed on the basis of the experimental data for bond length of H₂O molecule in a gas phase [12]. The fixed electric charges are attributed to H atoms and to the point M which is situated on the bisector of HOH angle at the distance of 0.0215 nm from the center of the oxygen atom. Values of charges and position of the point M are chosen so that to reproduce both the experimental values of dipole and quadrupole moments [13, 14] and *ab initio* calculated energy of a dimer and its characteristic distances [15]. Besides the electric charge, the polarizability required for the description of polarizing energy is related to this point M , too.

Total interaction energy of the system formed by water molecules consists of two terms

$$U_{\text{tot}} = U_{\text{pair}} + U_{\text{pol}}, \quad (1)$$

where the pair-additive part of potential is the sum of Lennard–Jones and Coulomb interactions

$$U_{\text{pair}} = \sum_i \sum_j \left(4\varepsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right). \quad (2)$$

Here r_{ij} is the distance between the atoms i and j ; q is a charge; σ and ε are the parameters of Lennard–Jones potential.

The polarization energy is defined by the relation

$$U_{\text{pol}} = -\frac{1}{2} \sum_i \mathbf{d}_i \mathbf{E}_i^0, \quad (3)$$

where \mathbf{E}_i^0 is the electric field strength at the atom i produced by all fixed charges of a system:

$$\mathbf{E}_i^0 = \sum_{j \neq i} \frac{q_j \mathbf{r}_{ij}}{r_{ij}^3}, \quad (4)$$

\mathbf{d}_i represents here the induced dipole moment of the atom i that is defined as

$$\mathbf{d}_i = \alpha_i \mathbf{E}_i, \quad (5)$$

where

$$\mathbf{E}_i = \mathbf{E}_i^0 + \sum_{j \neq i} \mathbf{T}_{ij} \cdot \mathbf{d}_j. \quad (6)$$

Here \mathbf{E}_i designates the total strength of electric field in a position of the atom i ; α is atomic polarizability; \mathbf{T}_{ij} — dipole tensor:

$$\mathbf{T}_{ij} = \frac{1}{r_{ij}^3} \left(\frac{3\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2} - 1 \right). \quad (7)$$

The standard iterative procedure is used to calculate the induced dipole moments at each time step. It consists of the following steps: a) by using equation (4), the strength of the electric field caused by fixed charges of the system is calculated in the point i ; b) the calculated strength of the electric field is then used in equation (5) to generate the initial estimated values of the induced dipole moments; c) according to equation (6), the new value of strength of the total electric field is calculated finally. Steps (b) and (c) are repeated until the change in the induced dipole moments between two consecutive iterations does not become less than the value we have previously set. The accuracy of definition of \mathbf{d}_i is taken usually in 10^{-5} - 10^{-4} D range [4].

To integrate the movement equations for the mass centers of molecules the Geer's method of the fourth order [16] is used. The time step of integration, Δt , was 10^{-17} s. The initial equilibrium state of a system was prepared at $T = 233$ K by

using the molecular dynamics simulation during $10^6 \Delta t$. Further evolution time varied from 10 ps up to 30 ps, i.e. one is equal $(1-3) \times 10^6 \Delta t$ for each cluster, so the number of the configurations used for calculation of thermodynamic properties reached three million. The analytical solution of the movement equations for the molecule rotation is carried out with Rodrigues - Hamilton parameters [17], and the integration method for the equations of movements in the presence of rotations corresponded to the approach offered by Sonnenschein [18]. Note that the obvious accounting for rotational movement of molecules is very important in modelling aqueous systems, since it improves the ergodic property of the system. During 1-3 million time steps, the system passes through a wide set of various structures with close energies. Calculations were made on a PENTIUM-IV computer with processor clock frequency 1.7 GHz. To calculate the cluster of 90 molecules during $10^6 \Delta t$ we spent about 180 h of computer time.

CRITERIA OF STABILITY

Thermodynamic equilibrium is provided by a maximum of entropy or by a minimum of one of the thermodynamic potentials. The most important isodynamic coefficients of stability are the combinations [19]: $\frac{T}{c_P}$, $-\left(\frac{\partial P}{\partial V}\right)_T$, $\frac{1}{\chi_{P,T}}$, and

$\frac{1}{\epsilon_{P,T}}$, where T is temperature, P — pressure; V — volume of system, c_P is its heat capacity at constant pressure; χ is the

magnetic, and ϵ is dielectric permeability. Subscript indexes P and T at values of χ and ϵ specify that double differentiation of internal energy U with respect to magnetic, \mathbf{B} , and electrostatic, \mathbf{I} , inductions is done at constant pressure and temperature:

$\left(\frac{\partial^2 U}{\partial \mathbf{B}^2}\right)_{P,T} = \frac{1}{\chi_{P,T}}$, $\left(\frac{\partial^2 U}{\partial \mathbf{I}^2}\right)_{P,T} = \frac{1}{\epsilon_{P,T}}$. Thermal and mechanical criteria of stability can be presented in the form of the

following inequalities:

$$\frac{T}{c_P} > 0, \quad (8)$$

$$-\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\beta_T V} > 0. \quad (9)$$

Criteria (8), (9) can be used for the analysis of stability both for extensional systems and systems with the limited number of degrees of freedom.

The total dipole moment of a cluster is set in the form of

$$\mathbf{M}(t) = Z_H \sum_{i=1}^{2N} \mathbf{r}_i(t) + Z_O \sum_{i=1}^N \mathbf{r}_i(t), \quad (10)$$

where $\mathbf{r}_i(t)$ is a vector specifying the position of the atom i at the time t ; Z is the electric charge placed into the center of the atom; index H relates to the hydrogen atom, and O relates to the oxygen atom; N is the number of water molecules in the cluster.

The optical dielectric constant is defined by the expression [20]

$$\epsilon_0 = 1 + \frac{4\pi}{3Vk_B T} [\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2]. \quad (11)$$

Dielectric constant, $\epsilon(\omega)$, is found from the equation

$$\frac{\epsilon(\omega) - 1}{\epsilon_0 - 1} = - \int_0^{\infty} \exp(-i\omega t) \frac{dF}{dt} dt = 1 - i\omega \int_0^{\infty} \exp(-i\omega t) F(t) dt, \quad (12)$$

where $F(t)$ means the normalized autocorrelation function of the total dipole moment of a cluster:

$$F(t) = \frac{\langle M(t) \cdot M(0) \rangle}{\langle M^2 \rangle}. \quad (13)$$

In general case, the connection between the external electric field $E(\omega)$ and the average dipole moment M originated by its influence, $M(\omega)$, is given by the expression [20]:

$$M(\omega) = \frac{i\omega}{4\pi} [1 - \varepsilon(\omega)] E(\omega). \quad (14)$$

Indexes P and T for the dielectric permeability in expression (14) are omitted.

Since the dielectric permeability can be presented as

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega), \quad (15)$$

then the stability of a cluster in relation to changes of the electric field is defined by the value $\varepsilon''(\omega) \cdot \omega / 4\pi$ which plays the role of the generalized susceptibility. The inverse value is the coefficient of dielectric stability. Then the condition of stability in relation to perturbations of the electric field in a cluster looks like this:

$$4\pi / [\varepsilon''(\omega) \cdot \omega] > 0. \quad (16)$$

The feature of this condition consists in that the stability of a dielectric state depends on the frequency of collective vibrations of molecules, while in the presence of an external field it depends on the frequency of electromagnetic vibrations. It is expedient to consider the feasibility of condition (16) with the certain characteristic frequency. The frequency corresponding to the maximum value of $\varepsilon''(\omega)$ was chosen as this value.

RESULTS OF CALCULATIONS

Water clusters containing a number of molecules $n \geq 6$ are characterized by a wide set of structured units close in energy, but different in topology [22]. Calculated total energy of clusters, U_{tot} , is displayed in Fig. 1. For the convenience of analyzing the function $U_{\text{tot}}(n)$ behavior, the values calculated by the molecular dynamics method (points) are approximated by a polynomial (curve 2). In comparison, the results of Monte–Carlo calculations of the same value, U_{tot} , for water aggregates with the intermolecular interaction represented by pairwise additive potential [21] are shown therein. One can see a satisfactory agreement between the total energy of clusters calculated for polarized (the present work) and non-polarized models of water. The difference between the calculated values of U_{tot} in these two models enlarges, when the cluster size

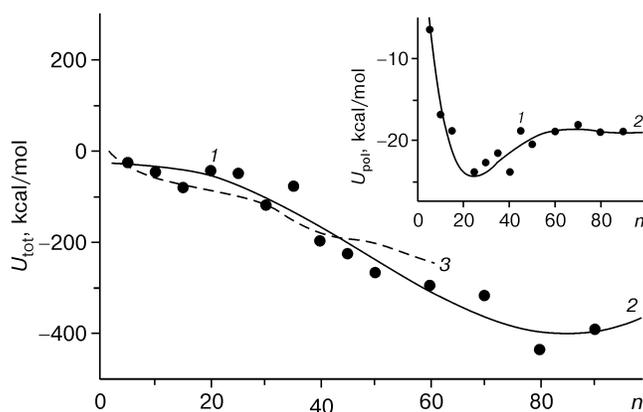


Fig. 1. Total and polarization energy (insert) of water clusters. 1 — the advanced TIP4P model, 2 — the fitting polynomial interpolating calculated data, 3 — non-polarized model [21].

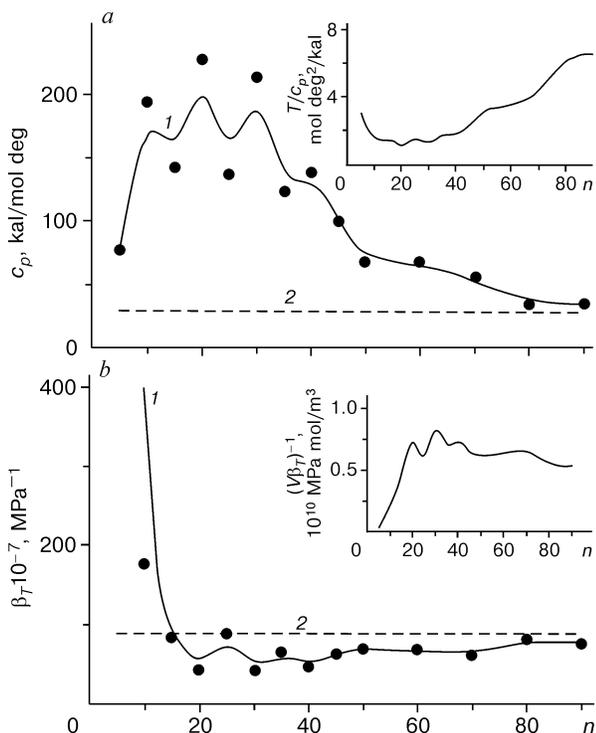


Fig. 2. Isobaric heat capacity (a) and isothermal compressibility (b) of water clusters. 1 — the advanced TIP4P model; 2 — the experiment [23]. Inserts: isodynamic coefficients of stability.

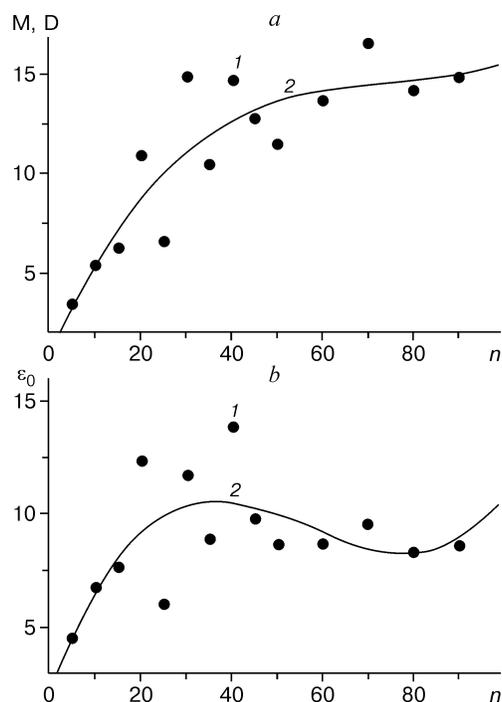


Fig. 3. The total dipole moment (a) and static dielectric permeability (b) of water clusters. 1 — advanced TIP4P model; 2 — a polynomial fitting data of the present calculations.

exceeds 50 molecules. Use of polarizable model in this case leads to lowering values of the energy, U_{tot} . The contribution from the energy of polarization, U_{pol} , to the total energy of clusters is the most noticeable in the range of their sizes $15 \leq n \leq 40$ (see insert in the top part of Fig. 1). At $n > 40$, the value of U_{pol} practically does not change with the growth of a number of molecules in the aggregate.

Thermal and mechanical stability of the system is defined by the second derivatives of the thermodynamic potential related accordingly to values of c_p and β_T . The isobaric heat capacity in our model has high values in a wide area of the sizes of clusters $(H_2O)_n$ (Fig. 2a). However, with the increase in number n , after passing several peaks, the heat capacity of the clusters c_p do decrease, gradually approaching the experimental value of a heat capacity of water [23] at similar temperature (233 K). The behaviour of the corresponding criterion of stability is represented as an insert in the right top corner of Fig. 2a. Initially, the thermal criterion of stability decreases with the number n increasing. Further it becomes oscillating and, at last, starting from $n = 40$, it increases steadily, thus reflecting the increase in the thermal stability of the largest clusters. Isothermal compressibility of clusters quickly decreases on the increase in the cluster size n from 5 up to 20 (see Fig. 2b). Then after few oscillations, the function $\beta_T(n)$ slowly approaches the experimental value of bulk water at $T = 233$ K [23]. The mechanical criterion of stability is presented as an insert in Fig. 2b. The quick increase in the mechanical stability accompanies the growth of the aggregate size n from 5 up to 20. Further, $(V\beta_T)^{-1}(n)$ has oscillating character and diminishes when the value of n exceeds 70. According to the calculated criterion of $(V\beta_T)^{-1}$, the cluster of 20 water molecules turns out to be more steady in vacuum than the aggregate of 90 molecules. The change of the total dipole moment with the increasing size of the aggregate is shown in Fig. 3a. One can see that M value increases rapidly with the growth of the number n , until the cluster size reaches $n = 40$. Then the growth of the function $M(n)$ slows down, but does not stop even at $n = 90$. Static dielectric constant ϵ_0 also sharply increases from the beginning (see Fig. 3b), passes through the maximum ($\epsilon_0 = 13.9$ at $n = 40$), and then decreases and

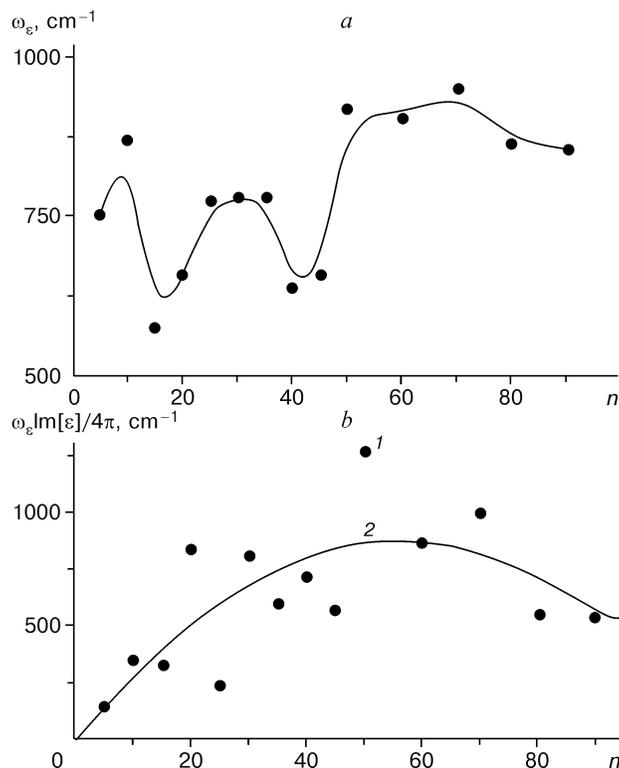


Fig. 4. The frequency corresponding to a maximum of an imaginary part of the dielectric permeability (a) and the criterion of the dielectric stability (b) of water clusters. Designations as in Fig. 3.

has a minimum ($\epsilon_0 = 8.4$ at $n = 80$). The experimental value for bulk water equals $\epsilon_0 = 78.6$ at $T = 298$ K [24]. Frequencies ω_ϵ corresponding to the maxima values of the imaginary part, ϵ'' , of the dielectric permeability are shown in Fig. 4a for the water clusters in question. Minimal (~ 577 cm^{-1}) frequency, ω_ϵ , at which dielectric properties are perturbed most strongly, corresponds to a cluster with $n = 15$, and maximal (~ 954 cm^{-1}) corresponds to the aggregate with $n = 70$. The behavior of dielectric stability criterion for the clusters with different numbers of molecules is shown in Fig. 4b. Among the considered clusters, the aggregate with $n = 5$ possess the least stability to electric perturbations with the frequency $\omega_\epsilon = 750$ cm^{-1} , while the cluster with $n = 50$ ($\omega_\epsilon = 922$ cm^{-1}) is most stable.

CONCLUSION

We have investigated the stability of water clusters containing up to 90 molecules. The use of the advanced TIP4P model of water with the polarization contribution to energy leads to a satisfactory agreement with the total energy of clusters calculated for the non-polarized model of water with simple additive interaction [21]. Isodynamic criteria of stability show that the thermal stability of clusters $(\text{H}_2\text{O})_{n \geq 10}$ grows with the increase in their size, and the mechanical stability having reached a high level fluctuates in the range of $20 \leq n \leq 70$, but begins to go down a little, when the cluster size transcends $n > 70$. The thermal criterion of stability with the reference to real clusters seems to be more reliable, as the value of the mechanical criterion should be appreciably affected by the environment of clusters (water vapor), which is not included in the present model. The total dipole moment of the clusters continuously increases with their size. The static dielectric constant has the value nearby $\epsilon_0 = 9.0$, when the cluster size reaches the value $n = 45$. Maxima of an imaginary part of the dielectric constant $\epsilon(\omega)$ shift to higher frequencies in the form of aperiodic oscillations with the increasing size of investigated water aggregates.

The criterion of dielectric stability indicates that the maximal stability to high-frequency electric perturbations is inherent to the cluster with a size of $n = 50$.

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