Rarefied Gas Dynamics: Experimental Techniques and Physical Systems

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Volume 158
PROGRESS IN
ASTRONAUTICS AND AERONAUTICS

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Molecular Clusters in Water and Intramolecular Vibration Spectra: A Molecular Dynamics Simulation Study

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Abstract

Molecular dynamics simulation runs of water at various densities are evaluated to detect structural units which are embedded in the random hydrogen bond network and which are characteristic building units of cubic and hexagonal ice crystals. We observe a strong increase of such units, when the mechanical stability limit is approached. To describe the shifts and narrowings of intramolecular vibration bands, which are produced by the observed structural changes, we calculate statistical characteristics of the forces acting as perturbation on the internal oscillators.

Introduction

Intramolecular vibration spectra, employed to investigate the formation of ice clusters from the vapor phase, have been presented frequently at this symposium. We extract information on such spectra from molecular dynamics simulations, using a method proposed by Postma, et al.[1] This method is based on the computation of the external forces which act as perturbations on the intramolecular oscillators, and which can be applied even when models of rigid molecules are used in the simulations.

The interaction between water molecules is dominated by their ability to form hydrogen bonds. It is well-known that the O-H stretching frequency of the partially deuterated water molecule HDO is very sensitive

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to this. The corresponding spectral band shifts by about 16% when the environment of the water molecule is changed from vapor to ice.

In accordance with this observation, we study the changes in the fundamental vibration spectra of water molecules, which are expected, when water is in a stretched, low–density metastable state. It has been shown before that this state is highly ordered, incorporating numerous ice–like molecular arrangements.[2] The occurence of the corresponding structural units, characteristic of hexagonal and cubic ice, are determined by calculating the pair distribution of hydrogen bond rings.[3] During the transformation from normal- to low–density water, a strong increase of such structural units is observed, and simultaneously a narrowing and shift of the distribution of the perturbing forces, which in turn produces a corresponding change of the intramolecular vibration band.

Simulation Outline

In a Molecular Dynamics (MD) simulation, the classical equations of motion of an N particle system

$$m_i \ddot{\mathbf{r}}_i = -\nabla_i V(\mathbf{r}_1, \ldots, \mathbf{r}_N) \qquad (i = 1, \ldots, N) \qquad (1)$$

is solved numerically. In most cases it is sufficient to apply the simple Verlet integration algorithm[4]

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) - \frac{(\Delta t)^2}{m_i} \nabla_i V \qquad (2)$$

The total potential energy $V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ of the N particle system is approximated by a decomposition into pair contributions

$$V(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i<j} V_2(\mathbf{r}_i, \mathbf{r}_j) \qquad (3)$$

To treat systems of rigid molecules, constraining forces have to be introduced, which preserve the constant intramolecular atomic distances. The action of such constraining forces is implemented in the simulation program by the so–called SHAKE algorithm.[5]

In this algorithm in a first step new positions $\mathbf{r}'_i(t + \Delta t)$ are calculated without the action of any constraining force. In a second step, SHAKE calculates iteratively the necessary shifts $\delta\mathbf{r}_i$ to get the correct atomic positions

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}'_i(t + \Delta t) + \delta\mathbf{r}_i \qquad (4)$$

including bond length and bond angle constraints. $\delta\mathbf{r}_i$ is proportional to the intramolecular forces, which keep the shape of the molecule fixed. These forces reflect the molecular environment, especially the H–bond interactions between neighboring molecules. They also act as a pertubation of the an-
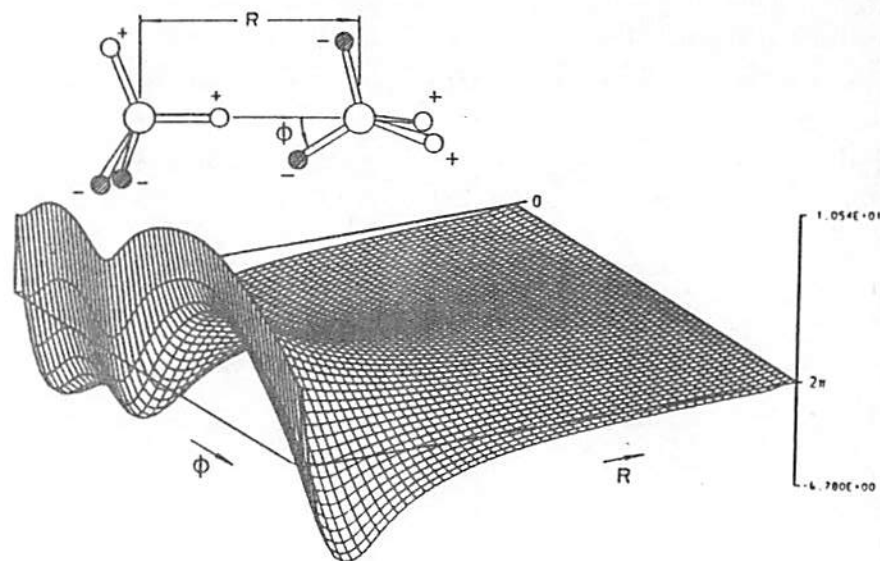
Fig. 1   Interaction energy of two water molecules as a function of distance and orientation, as described by the ST2 potential model of the simulation.

harmonic intramolecular oscillators and therefore cause oscillator frequency shifts.

Postma et al.[1] showed that this shift is proportional to the magnitude of the displacement $\delta\mathbf{r}_i$. Thus, the distribution of displacements, obtained in the simulation, reflects the experimentally observable inhomogeneous broadenings and shifts of the spectral lines in the condensed phase.

In our simulations we use the so–called ST2 potential.[6] This describes the effective pair interaction energy of two water molecules in the condensed phase as a function of their distance and mutual orientation, as illustrated in Fig. 1.

To change (increase) the number of ice–like clusters in the simulated water, in a series of simulation runs at constant temperature ($T \approx 273$ K) we gradually decrease the density of the liquid from $\rho = 1.0$ to 0.7 g/cm^3, corresponding to the application of increasingly negative pressures (stretching forces). Details of the simulation are given in.[2] There it was shown that in the metastable, stretched water the liquid is more and more ordered. Moreover, these studies showed that at $\rho = 0.8$ g/cm^3 (and $T = 273$ K) a limit of mechanical stability is reached, which can be related to the structural changes in the hydrogen bond network.

Ice-Like Clusters in the Liquid Phase

The interaction between water molecules is dominated by the occurence of hydrogen bonds, which form a macroscopic, space-filling network in the
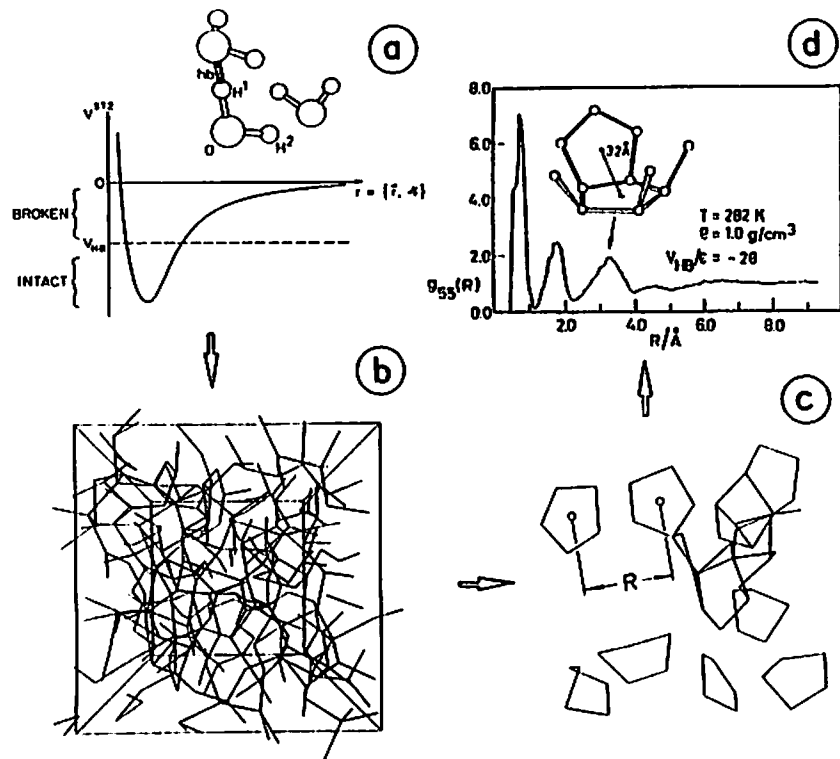
Fig. 2   Procedure to identify ice-like structural elements: a) definition of the hydrogen bond, b) snapshot of the random hydrogen bond network, c) distribution of pentagonal rings in the network, and d) pair correlation function of rings [here: $g_{55}(r)$].

liquid state. In the framework of the simulation studies, we define a pair of water molecules as hydrogen bonded when the pair interaction energy is more negative (stronger) than some suitably chosen[2] threshold value V_{HB} (Fig. 2a). Applying this definition to any water configuration, an infinite network, as illustrated in Fig. 2b, is obtained. Within this network, we find a variety of hydrogen bond rings, consisting of various numbers p of water molecules. These rings are identified, using a special searching routine.[7] For pentagonal rings ($p = 5$) a typical distribution is shown in Fig. 2c. Having identified the position of a ring by its center of mass, it is possible to calculate ring-ring pair correlation functions $g_{pp'}(R)$, when R is the distance between the centers of mass of the two rings of size p and p'. The pair distribution function $g_{55}(r)$ of pentagonal rings, as found for a bond threshold energy $V_{HB} = -2.2$ kcal/mole in water of density $\rho = 1.0$ g/cm³ is shown in Fig. 2d.
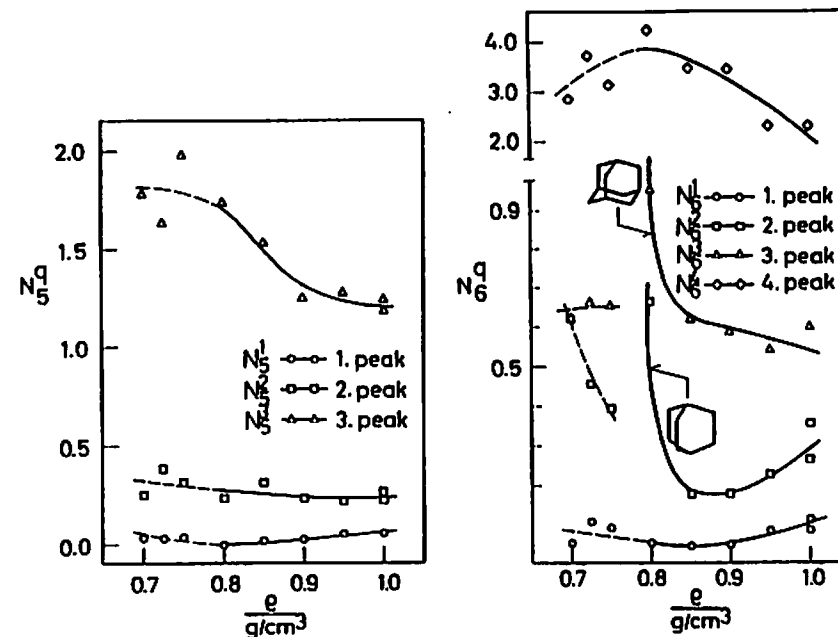

Fig. 3   Average number $N_p{}^q$ of structural elements with $p - (q + 1)$ common hydrogen bonds for pentagons ($p = 5$) and hexagons ($p = 6$). The threshold energy is chosen here to $V_{HB} = -3.0$ kcal/mol.

The qth peak of the pair correlation function $g_{pp}(R)$ is produced by pairs of rings, which have $p - (q+1)$ common bonds. For example, the third peak ($q = 3$) of $g_{55}(R)$ at $R = 3.2Å$ is due to a pair of pentagonal rings which share one common bond. A more detailed description of this approach is given in Ref. 3.

Integration of the various peaks yields the average number $N_p{}^q$ of the corresponding structural elements. By this method, the growth of various structural elements can be monitored when penetrating into the metastable region of the liquid. This is shown in Fig. 3 for pentagonal ($p = 5$) and hexagonal ($p = 6$) ring units. It can be seen that in particular the structural elements, which consist of fused hexagons with two (in the case of $N_6{}^3$) and three ($N_6{}^2$) shared bonds, increase dramatically as they approach the limit of mechanical stability at $\rho = 0.8$ g/cm³. These elements can be identified as building blocks for the hexagonal and cubic ice lattice. This strongly indicates the occurence of a spinodal phase transformation, which is only prevented by the finite size of our simulated systems and the finite length of the simulation runs.

Intramolecular Vibration Spectra

The discussed structural changes (increase of ice-like clusters in the stretched water region) should be detectable in vibration spectra. Therefore,
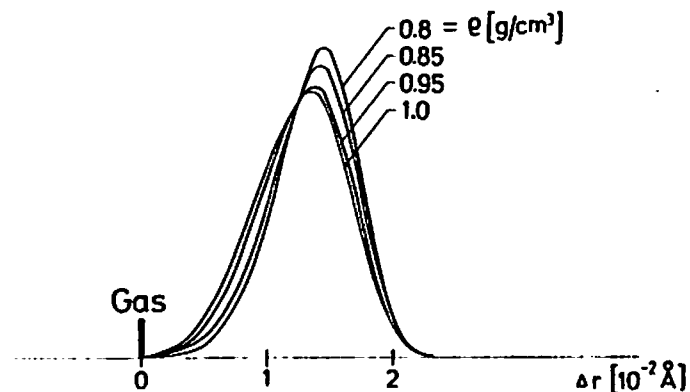
Fig. 4   Distribution of displacements δr_i, representing the line shifts and inhomogeneous line broadenings due to the structural changes in metastable water.

in Fig. 4 we give the distribution of displacements δr_i. As discussed in the "Simulation Outline", these distributions reflect the line shifts and line broadenings, which are results of the variation of the environment of the water molecules.

The increasing shift with decreasing density is produced by an increasing number of strong hydrogen bonds, whereas the decrease of the linewidth reflects an increasing local order. This is in agreement with the conventional interpretation of the temperature dependence of infrared and Raman spectra of HDO.[8]

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