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" Mobility of Stretched Water."

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To study the mobility of stretched SPC/E water and its dependence on temperature and density we performed five molecular dynamics computer simulation runs. Three runs were performed at temperature 300 K and densities 1.0 g/cc, 0.9 g/cc and 0.8 g/cc. Two more runs were performed at temperature 273 K and densities 1.0 g/cc and 0.9 g/cc. At temperature 300 K the translational diffusion coefficient of the stretched SPC/E water increased with the stretch, at temperature 273 K the translational diffusion decreased with the stretch. This behavior is correlated with the observed changes in the hydrogen bonding pattern of water.

Mobility of Stretched Water.

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ABSTRACT

To study the mobility of stretched SPC/E water and its dependence on temperature and density we performed five molecular dynamics computer simulation runs. Three runs were performed at temperature 300 K and densities 1.0 g/cc, 0.9 g/cc and 0.8 g/cc. Two more runs were performed at temperature 273 K and densities 1.0 g/cc and 0.9 g/cc. At temperature 300 K the translational diffusion coefficient of the stretched SPC/E water increased with the stretch, at temperature 273 K the translational diffusion decreased with the stretch. This behavior is correlated with the observed changes in the hydrogen bonding pattern of water.

INTRODUCTION

Experimental data on stretched water are hard to obtain^{1,2}. Therefore, one should expect that in this area computer modelling will play a rather important role³. Recent computer simulations revealed that water mobility displays an anomalous behavior under stretch, i.e., the rotational and translational single particle diffusion slowed down when the density of water was reduced^{4,5}. The anomalous behavior of the translational and rotational diffusion coefficients is observed in experiments with condensed water⁶. These experiments show that the anomaly in water mobility is temperature dependent. At temperatures below ~300 K the initial compression of water results in increase of its mobility. Further compression leads to the return of normal behavior. At temperatures above 300 K the anomaly in translational diffusion is not observed and water behaves as a normal fluid. This peculiar behavior that water displays under compression was also seen in a computer simulation⁷. It would be interesting to find out if the mobility of stretched water shows the same kind of normal/abnormal behavior as a function of temperature. Indeed, since there is nothing special about the density of 1 g/cc, one should expect to observe normal behavior in the mobility of water under initial stretch at temperatures above ~300 K (see Fig 1). Eventually, the change in the mobility from a normal to an abnormal behavior should occur at some density point. The location of this point is not known, but one should expect that it moves towards higher density when the temperature decreases (Fig. 1). Therefore at temperatures below ~300 K the behavior of the diffusion coefficient for stretched water is expected to show an abnormal character. Indeed, Sciortino et al.^{4,5} observed only this type of behavior in their molecular dynamics simulations, since these were performed at temperatures below 300 K.

METHODS

To study the mobility of the stretched water and its temperature and density dependence, we performed five molecular dynamic computer simulation runs. Three runs were performed at $T=300$ K and at densities 1.0 g/cc (run 1), 0.9 g/cc (run 2) and 0.8 g/cc (run 3). The other two runs were performed at $T=273$ K and at densities 1.0 g/cc (run 4) and 0.9 g/cc (run 5). All calculations were done on 216 water molecules in a cubic box with periodic boundary conditions in NVT ensemble.

The equations of motion were integrated using a leap-frog algorithm with a time step of 2.5 fs. The temperature was kept constant by coupling to an external heat bath⁸ with a relaxation time constant of 0.05 ps. The SHAKE procedure⁹ was used to constrain the internal geometry of water molecules. The potential energy of the interaction between two water molecules was multiplied by the switching function proposed by Steinhauser¹⁰, which smoothly reduces the energy from its value at $R_T=0.874$ nm to zero at $R_C=0.92$ nm. The contribution of the long range forces was taken into account using the reaction field method.

Simulation systems with densities 0.9 g/cc and 0.8 g/cc were prepared by 'stretching' the normal density water box, i.e. all oxygen coordinates were scaled by factor of 1.036 and 1.077 respectively. Then each system was equilibrated for at least 50 ps.

For the water-water intermolecular interactions the SPC/E potential¹¹ was used. The SPC/E model provides an accurate estimate of a number of physical properties of liquid water. Although, potential parameters were adjusted at normal density and the behavior of SPC/E water at low densities is not known, we can expect at least qualitative consistency of simulation results.

RESULTS AND DISCUSSIONS

To calculate the self-diffusion coefficient of water we used the Einstein equation:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \langle |R(t) - R(0)|^2 \rangle \quad (1)$$

where $R(t)$ is the position of the center of mass of water molecule at time t and $R(0)$ is the initial position of this molecule. Since the relaxation of the simulated system is very slow, especially at low temperatures and/or densities, calculation of D required long runs. We calculated D in sequential intervals of 50 ps until we achieved reasonable values in fluctuations of D . Actually the fluctuations in the values of D obtained from the last three sequential intervals of 50 ps never exceeded 5 %. In Table 1 we list the values of the diffusion coefficients which were obtained from the last 150 ps of each run. We want to note here that the temperature dependence of self-diffusion coefficient of SPC/E water at normal density is in a good agreement with experimental results¹² ($D_{300} = 2.41 \cdot 10^{-5} \text{ cm}^2/\text{s}$, $D_{273} = 1.33 \cdot 10^{-5} \text{ cm}^2/\text{s}$).

Our results show that the density dependence of the diffusion coefficient of stretched SPC/E water is qualitatively different at different temperatures: at 300 K it increases as density decreases (normal behavior) while at 273 K the diffusion coefficient decreases with the decrease in density (abnormal behavior).

We shall now try to correlate the behavior of water diffusion with the change in water structure under stretch. In the previous simulations^{4,5} an attempt was made to correlate the mobility change with the change in the hidden structures of water¹³. Since hidden structures do not depend on temperature and our simulations show that the mobility is temperature dependent, our description of the changes in the structure should also be temperature

dependent.

It is customary to describe structural changes in the substance by looking at the changes in the radial distribution function (rdf), $g(r)$ (Fig. 2). Our results show that the intensity of the first peak of the oxygen-oxygen rdf increases with the density decrease, irrespective of the temperature. This increase is usually considered to be a sign of the structure build-up, but a more careful analysis of the concept of the rdf reveals that this is not so¹⁴. By the definition $g_{oo}(r)$ is given by the equation

$$g_{oo}(r) = \rho_{oo}(r)/\rho \quad (2)$$

where $\rho_{oo}(r)$ is the local density of oxygen around fixed oxygen and ρ is the bulk density of oxygen. When the density of water is reduced the local density at the position of the first peak is very slightly changed, since water is an associative liquid. Therefore it is the reduction of the bulk density under stretch that is responsible for the increase in the value of the rdf at its first maximum. That means that the appearance of the increase in the ordering of water reflected by the increase of the first maximum of the rdf is mostly due to the simple normalization factor.

We can try to describe the change in water structure under stretch by monitoring the change in the hydrogen bond (HB) network. Although any definition of HB is arbitrary and quantitative values of HB network parameters depend on chosen criterion, analysis of those values allow us to follow trends in network changes under different conditions. There are two widely accepted types of hydrogen bond criteria: geometric¹⁵ and energetic¹⁶. In this work we used a combined one: two molecules were considered as bonded if the interaction energy of the pair of water molecules was lower than -10 kJ/mol and when the distance between two

hydrogens was smaller than 0.33 nm. The distribution of the number of HB per water molecule is also displayed in Table 1.

In ideal ice all water molecules are four hydrogen bonded, whereas in liquid water the hydrogen bonded network has defects and therefore one can find other than four hydrogen bonded water molecules. Five hydrogen bonded molecules appear when bifurcation of the hydrogen bond takes place. According to Sciortino et al.⁵ the presence of these bifurcated bonds is instrumental in lowering the barrier for the translational motion. As the density of water is reduced the fraction of five hydrogen bonded water molecules is reduced, the structure of water becomes more ice-like and therefore the mobility of water is decreased. The same qualitative picture is observed in our simulation at temperature 273 K, where the number of four hydrogen bonded molecules is increased, while the number of five hydrogen bonded molecules is decreased when water is stretched (Table 1). When lowering the density at 300 K the number of five hydrogen bonded water molecules is again decreased, but so is the number of four hydrogen bonded molecules. This observation indicates that the tetrahedral character of the hydrogen bonding network is weakened at 300 K and therefore the mobility of water is increased.

The tetrahedral character of water structure can also be described in terms of the packing of the irregular polyhedra in what is called the "statistical geometry" approach.¹⁷⁻¹⁹ To measure the distortion of those polyhedra in water in our simulations we used the tetrahedrality index t .²⁰ To define the tetrahedrality index t consider any water molecule and its four nearest neighbors. The oxygens of these four neighbors are vertices of the tetrahedra we built around our central water molecule. The tetrahedrality index t is defined by the following equation

$$t = \sum_{i>j} |(l_i - l_j)| / 15l + \sum_k |(r_k - r)| / 4r \quad (3)$$

where l_i is the length of the i -th edge and l is the mean length of the edges, r_k is the distance between the oxygen of the central water molecule and the oxygens of the tetrahedron vertexes, and r is the mean distance between the center and vertexes. For the ideal tetrahedron t is equal to zero and t increases with the increase of the tetrahedron distortion. The distribution of this index is displayed in Fig. 3. As one can see from this figure the hydrogen bonded network becomes more tetrahedral when water is stretched at $T=273$ K. At $T=300$ K the tetrahedrality of the network decreases with stretching.

CONCLUSIONS.

Summarizing the results from our simulations we conclude that:

The translational diffusion coefficient of water does not always decrease with the density decrease. At high temperatures (above 300 K) stretched SPC/E water actually behaves as a normal fluid; its diffusion coefficient increases with the stretch. Such behavior is also expected to be observed in real water (Fig. 1).

The observed increase in amplitudes of the first neighbor peaks of the rdf for stretched water does not necessarily correspond to enhanced ordering of water. This increase is mostly due to the normalization factor.

The behavior of the diffusion coefficient is correlated to the behavior of tetrahedrality of the hydrogen bond network in water. Diffusion coefficient increases as the tetrahedrality decreases and decreases as the tetrahedrality increases.

Translational diffusion of water depends on density and temperature, and this dependance is rather subtle. We therefore believe that it is not possible to explain the

mobility of stretched water in terms of hidden structures only, which are independent of temperature.

And finally, we want to emphasize again that since we do not know how well the SPC/E potential describes the properties of stretched water, one should understand that the calculated diffusion coefficients of low density water may differ from the values to be obtained from experiment. It is very possible that other models of water such as TIP4P²¹ or ST2²² may perform quantitatively better at lower densities. But our goal in the present work was to establish a connection between the abnormal and normal behavior of water mobility on one side and the hydrogen bonding pattern on the other side. In addition we wanted to clarify the usefulness of certain concepts used to describe the structural changes in water under the changes in density. As it turned out, the SPC/E model performed satisfactory in helping us to achieve our goal.

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FIG. 1 A sketch that represents the qualitative behavior of the diffusion coefficient as a function of density for different isotherms.

FIG. 2 Oxygen-oxygen rdf at 273 K (a) and at 300 K (b). Density 1.0 g/cc - solid line, 0.9 g/cc - dashed line, 0.8 g/cc - dotted line.

FIG. 3 Distribution for the tetrahedrality index of water at 273 K (a) and at 300 K (b). (Lines are as in Fig. 2).

T(K)	ρ	τ	D	N_{HB}	1	2	3	4	5	6
300	1.0	300	2.43	3.62	0.6	7.4	32.1	49.4	10.0	0.6
300	0.9	400	2.70	3.53	0.8	9.0	34.2	48.5	7.2	0.3
300	0.8	450	2.92	3.46	1.0	10.8	35.9	46.0	6.1	0.2
273	1.0	300	1.46	3.70	0.4	5.5	28.8	54.9	10.0	0.5
273	0.9	400	1.36	3.64	0.4	6.1	30.6	56.2	7.0	0.2

Table 1.

Temperature, density (ρ , in g/cc), run time (τ , in ps), diffusion coefficient ($D \cdot 10^5$, cm^2/s), and average number of hydrogen bonds per water molecule (N_{HB}) calculated from molecular dynamics (MD) runs. 1,2...6 in the first row stand for the one hydrogen bond per water molecule, two hydrogen bonds, etc. The diffusion coefficients and average number of hydrogen bonds per water molecule were calculated from the last 150 ps of the trajectories.

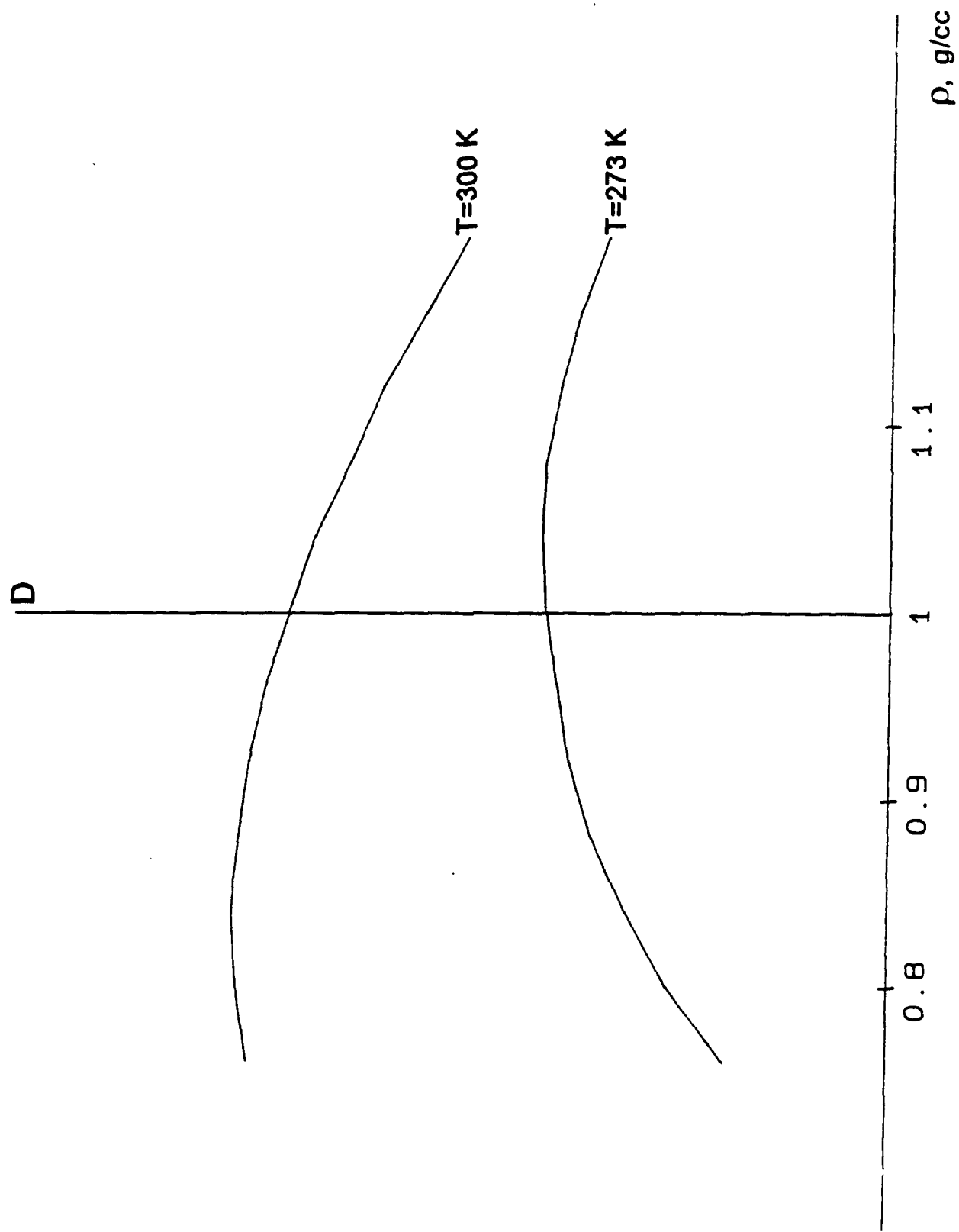


Fig. 1

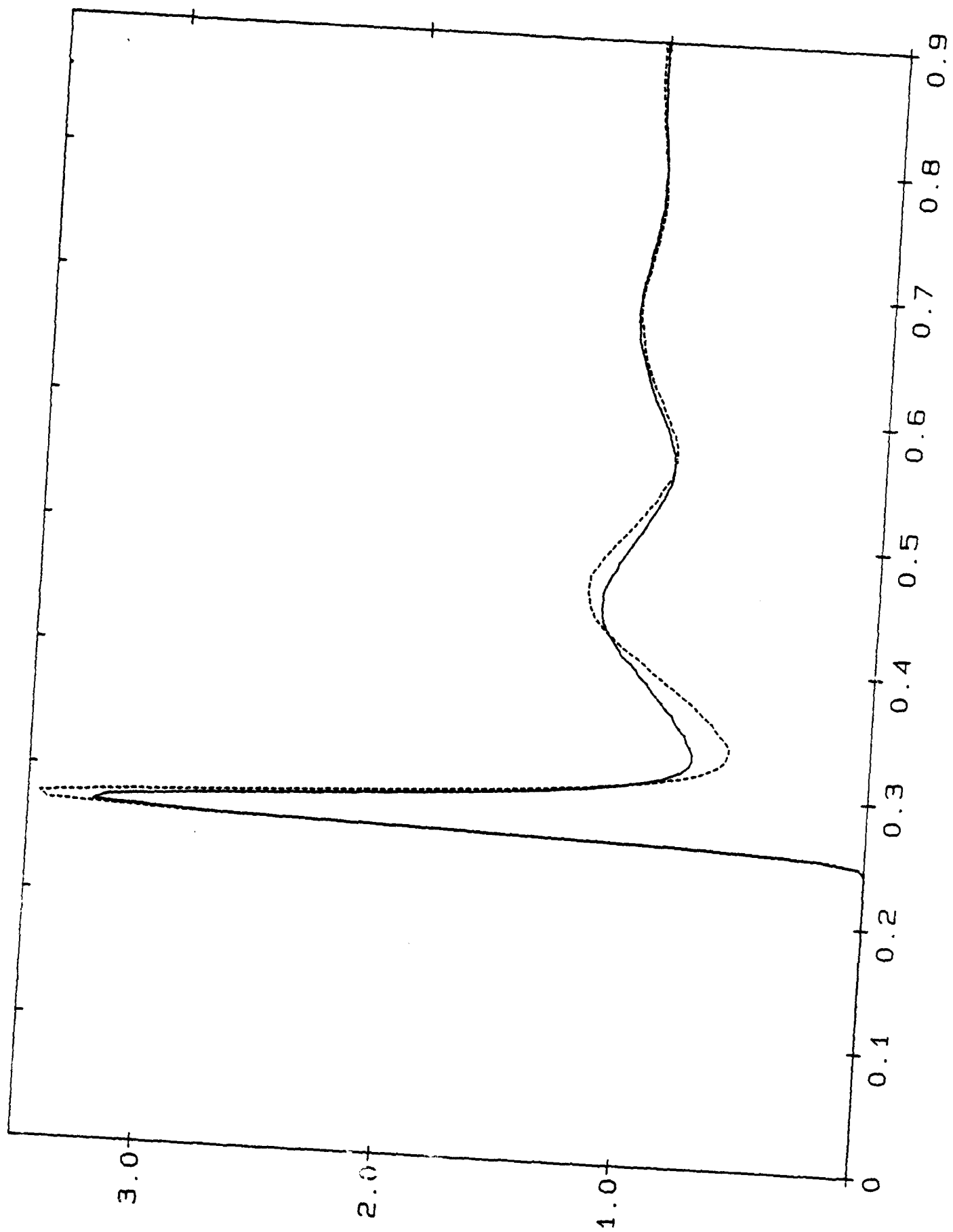


Fig. 2a

Fig. 2b

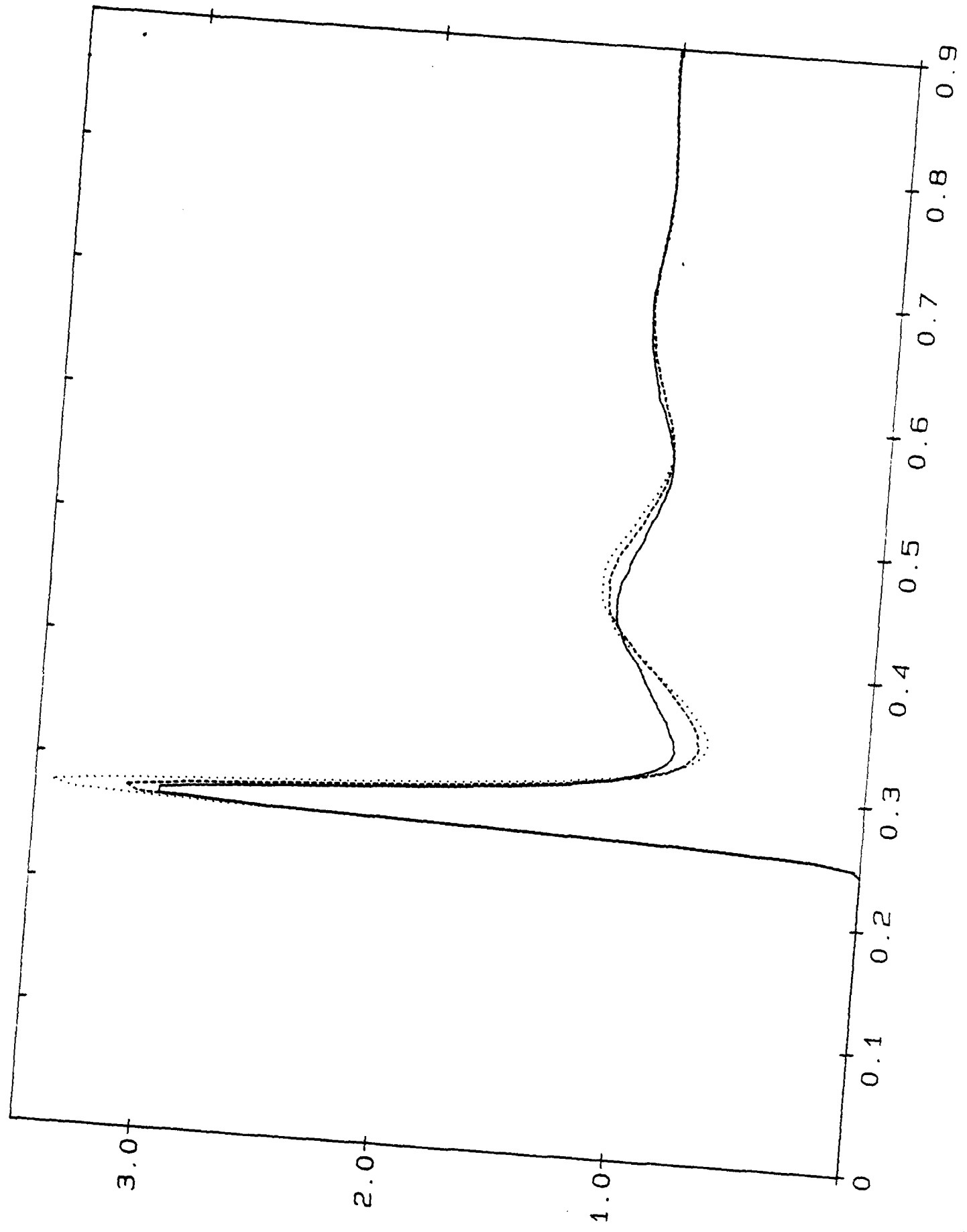


Fig. 3a

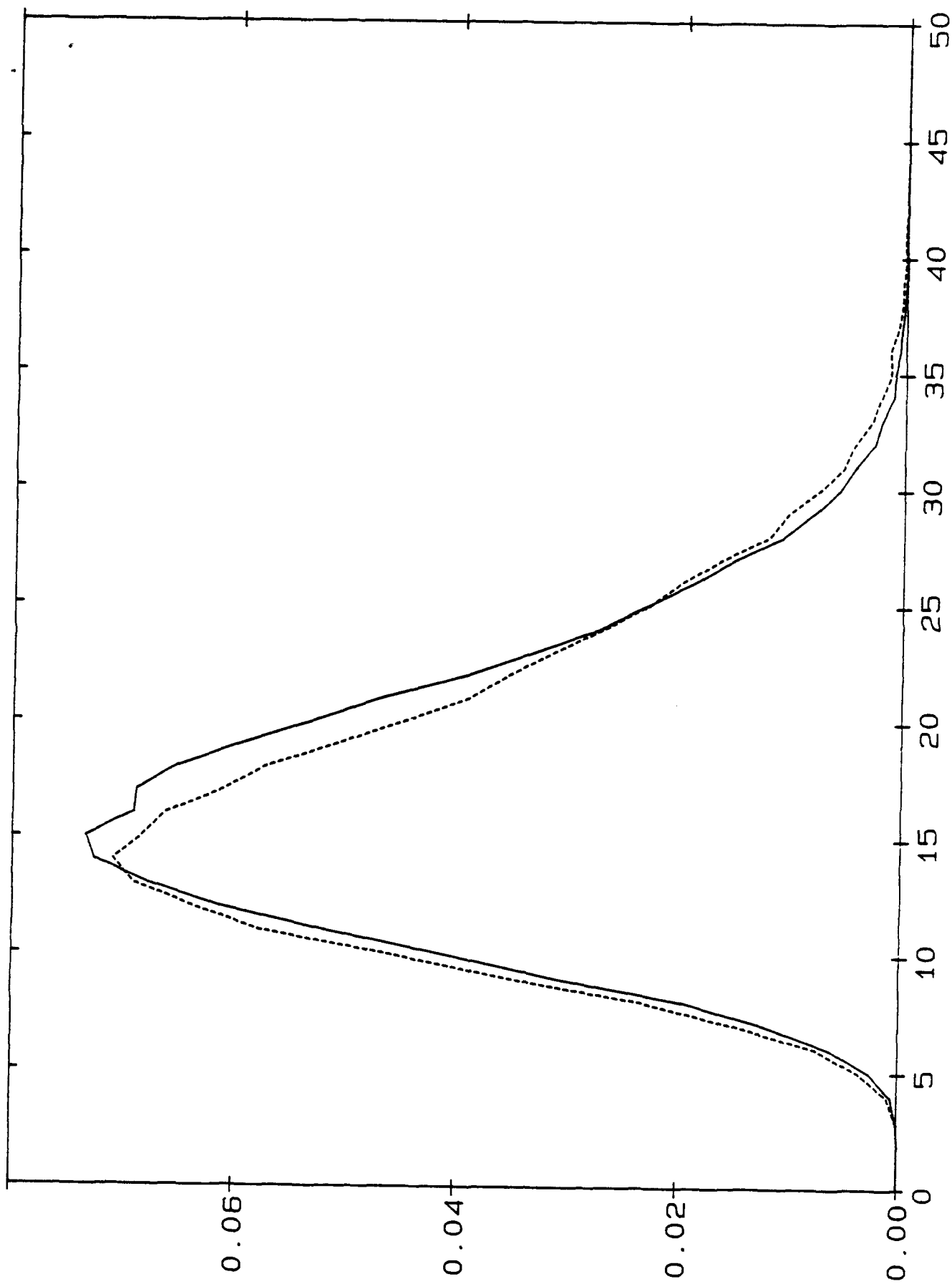


Fig. 3b

