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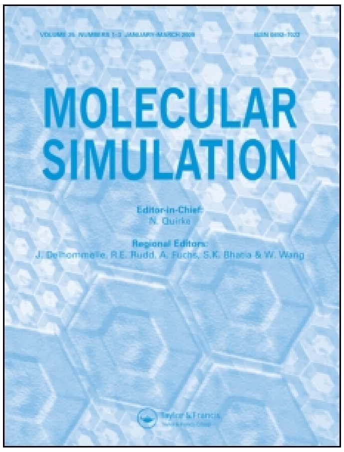

Molecular Simulation

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Molecular Dynamics Studies of Electrolyte Solution/Metal Interfaces

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MOLECULAR DYNAMICS STUDIES OF ELECTROLYTE SOLUTION/METAL INTERFACES

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The results of Molecular Dynamics simulations of pure water near a Pt(100) and a mercury surface as well as an aqueous LiI solution in contact with the Pt(100) surface are reported. The flexible BJH water model is employed in the simulations and the metal-water, ion-water and platinum-ion potentials are derived from molecular orbital calculations. It is shown that the structural and dynamical properties of water and the ions in the adsorbed water layer are significantly different from those in the bulk region.

KEY WORDS: Theory, computer simulation, interface, aqueous electrolyte solution, platinum surface, mercury surface.

1 INTRODUCTION

In the first attempts to describe realistically a water/metal interface the metal was considered to be a homogeneous dielectric medium with an infinitely high permittivity [1,2]. Therefore, the Coulomb interactions between the charged particles in the solution and the metal were described in terms of image charges, the non-Coulombic ones by Lennard-Jones (LJ)-potentials. In the case of the adsorbed water a strong preference for an orientation of the dipole moment parallel to the surface was found together with a symmetric distribution around the preferential orientation. This result has led to disagreement with work function measurements for water adsorption on several metal surfaces and with quantum mechanical calculations indicating an adsorption site at the top of a platinum atom in contradiction to the hollow site position found in the simulations [3].

Therefore, it seemed to be appropriate to try to find water-metal potentials which lead to better agreement between simulation on one side and experiments and *ab initio* calculations on the other. Consequently, the potential used by Spohr to describe the interaction between water and a Pt(100) surface [4] is based on extended Hückel molecular orbital calculations of a platinum cluster with a water molecule [5]. Further improvements have been achieved by employing a flexible model for the description of the water-water interactions [6].

With this new potential the properties of pure water at the Pt(100) surface were investigated in various simulations, including different degrees of coverage and charged walls [7]. All results demonstrate that the structural and dynamical properties of water near the surface are significantly different from those of the bulk region. The adsorbed water layer is rather rigid, and the translational motions of the water molecules are strongly reduced. The influence of the metal surface extends to the second and, much weaker, to the third water layer. Raghavan *et al.* [8] confirmed these results in a more recent MD study employing a similar potential for the Pt-water interactions and extended the investigations to the simulation of water near a Pt(111) surface.

In a similar way a potential describing the interaction between water and a mercury surface has been derived based on *ab initio* calculations of Nazmutdinov *et al.* [9]. First results of simulations with this potential have been reported recently by Böcker *et al.* [10].

This presentation will concentrate on the comparison of structural properties of water near a mercury and a Pt(100) surface as well as on results of MD simulations, which have been performed on aqueous LiI solutions in contact with a Pt(100) surface. In order to obtain a more reliable description of the ion-metal interactions the ion-platinum potentials were again derived from *ab initio* calculation of ion-platinum clusters [11]. Some properties of the hydration shells of Li^+or I^- located near the metal surface are compared with those in an bulk electrolyte solution [12].

2 INTERACTION POTENTIALS

The water-water potentials employed in the simulations are described by the flexible BJH model which has proved its usefulness in various simulations of pure water and aqueous electrolyte solutions [13]. The platinum-platinum and mercury-mercury interactions are modelled by a harmonic nearest-neighbour potential in order to account for the coupling between motions of the water molecules and lattice vibrations [14].

The analytical form of the platinum-water potential has been proposed by Spohr [4]. It is based on extended Hückel molecular orbital calculations of a water molecule and a five-atom platinum cluster by Holloway and Bennemann [5]. Figure la shows the quadratic arrangement of the platinum atoms on the (100) surface with a lattice constant of 2.77 Å. From the five atom platinum cluster used in the *ab initio* calculations four atoms belong to the first and one to the second layer. It has been cut out of the Pt(100) surface as indicated in Fig.1a. On the mercury surface the atoms are arranged rhombohedrally (Fig.1b). For the *ab initio* calculations only surface atoms were employed. The cluster used to study the adsorption of a water molecule consisted of seven mercury atoms for the case where the oxygen atom is positioned on top of a mercury atom while only six atoms are employed for hollow and bridge site positions [9]. The denotations top, bridge and hollow site for the mercury surface are explained in Fig.1b. For the Pt(100) surface the definitions apply accordingly. The parameterized potentials based on absorption energies of a water molecule on the mercury surface are presented in [10].

In Figure 2 the potential energies between a water molecule and the infinitely extended platinum (100) and mercury surface are depicted as a function of the

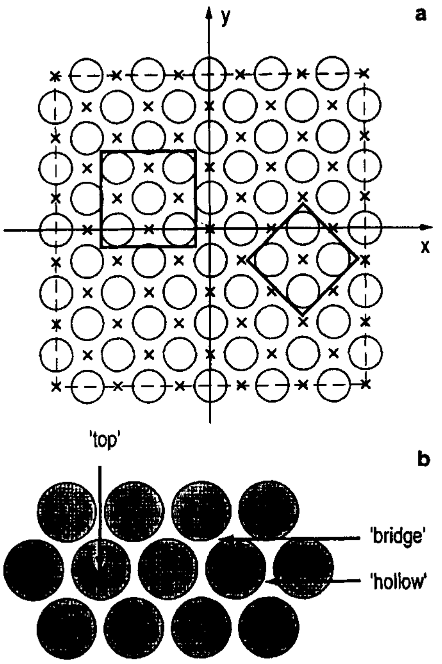

Figure 1 (a) Sketch of the arrangement of the platinum atoms in the first (circles) and second (crosses) layer of the (100) surface which coincides with the *xy*-plane of the basic periodic box the border of which is marked by dashed lines. Form and size of the two clusters used for the *ab initio* calculations are indicated. (b) Relative positions of the water molecules on the mercury surface. The denotations top, bridge and hollow site are used for the Pt(100) surface accordingly.

oxygen-surface distance z for different relative positions and orientations. Both potentials lead to the preferential adsorption site on top of a metal atom. The energetically most favourable orientation is the one where the dipole moment vector points away from the surface with a minimum of the total interaction energy of −35.7 and of −38.6 kJ/mol for the Pt and Hg surface, respectively. The potential minima for the mercury surface are found at distances about 0.5 Å larger than for the platinum surface. While the dependence of the energy on the relative orientation of the dipole moment vector is quite similar for both metals, the difference between top, bridge and hollow site is much smaller for the mercury compared with the platinum surface.

The platinum-$I^-$and platinum-Li^+ potentials are derived from molecular orbital calculations of one ion and a platinum cluster consisting of nine and five atoms, respectively [11]. Figure 3 shows that both ions are adsorbed preferentially opposite of a hollow site of the Pt(100) surface and the lowest potential minima for Li^+ and I^- are found at −265 and −319 kJ/mol, respectively. For further details of the potentials the reader is referred to the original publications cited.

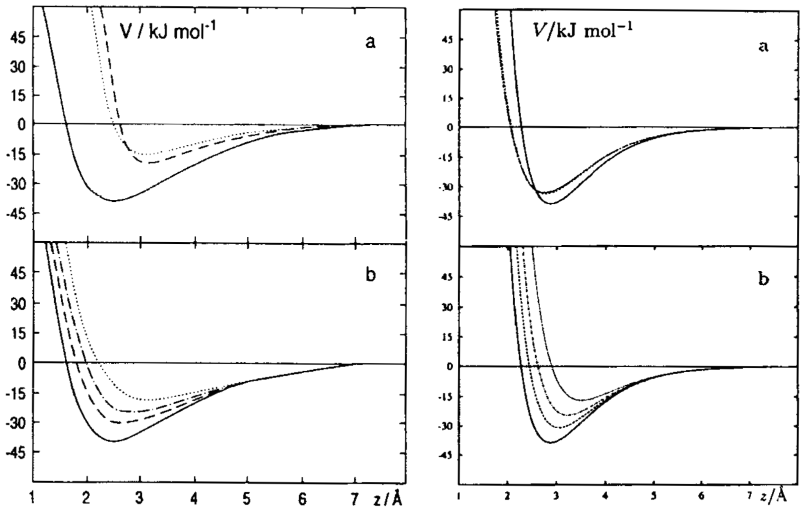

Figure 2 Water-platinum (left) and water-mercury (right) interaction potentials as a function of the oxygen-surface distance. (a) For water on top of a metal atom (full line), on a bridge site (dashed), and on a hollow site (dotted). The dipole moment vector of the water molecule points away from the surface in all three cases. (b) For different orientations of the dipole moment vector relative to the surface: pointing away (full), towards (dotted), and parallel with the proton-proton vector parallel (dashed) and perpendicular (dash-dotted) to the surface. In all four cases the adsorption site is on top of a metal atom.

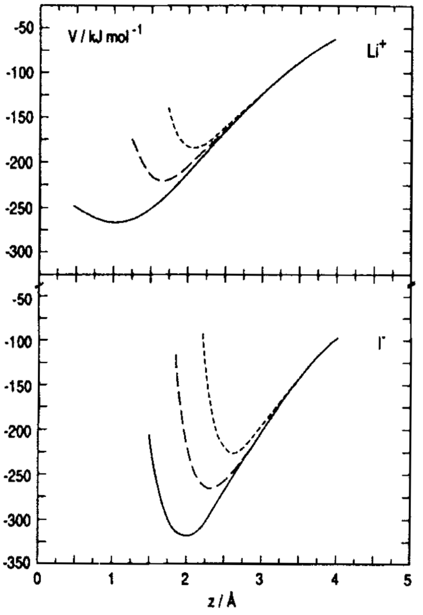

Figure 3 Potential energy of a lithium and an iodide ion as functions of distance from an infinitely extended Pt(100) surface for ion positions on top of a platinum atom (- - -), on a bridge site (– –) and a hollow site (——).

3 DETAILS OF THE SIMULATIONS

The rectangular basic box for the MD simulations of pure water and of the 2.2 molal LiI solution at the Pt(100) surface is shown in Figure 4. Between the five layers of platinum atoms on each side-altogether 550-remains space for about 6 layers of water molecules. In accord with the lattice constant for the Pt(100) surface the sidelengths of the rectangular box $L_x = L_y = 19.6$ Å and $L_z = 45$ Å result. The number of 305 water molecules between the two platinum surfaces was reached by adding water molecules until the density in the centre of the box became that of bulk water. In this way agreement with the usual experimental conditions was achieved. For the 2.2 molal LiI solution 298 water molecules, 10 Li^+ and 10 I^- filled the space between the platinum surfaces.

For the simulation of the mercury-water interface a similar rectangular box was chosen. The 440 mercury atoms on each side are arranged rhombohedrally with a nearest neighbor distance of 3 and 3.6 Å in the x, y and the z directions, respectively. 551 water molecules occupy the space between the two mercury surfaces. The resulting dimensions of the basic box are $L_x = 24$ Å, $L_y = 26$ Å and $L_z = 60.2$ Å.

In the x- and y-directions periodic boundary conditions have been introduced. In this way an infinitely extended water lamella between metal walls has been simulated. As long as no external electrical field is applied both interfaces are equivalent and the comparison of the results indicates the statistical significance of

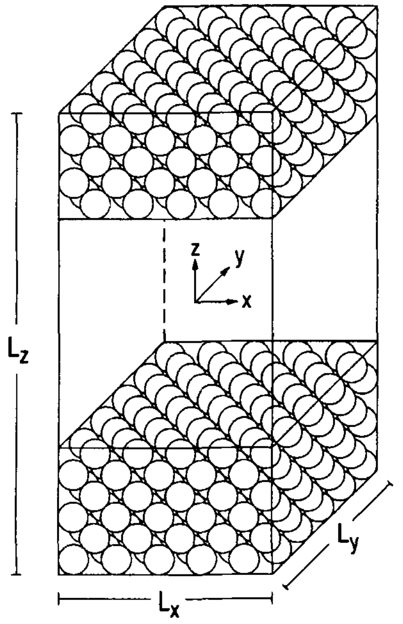

Figure 4 Sketch of the basic tetragonal simulation cell. The water molecules and the ions are located in the center of the box, and the platinum atoms are represented by the circles. The coordinate system which is used throughout the paper is inserted in the center.

the calculated properties. The simulations were performed at room temperature. For further details the reader is referred to the original papers cited.

4 RESULTS AND DISCUSSION

4.1 Density Profiles

The first properties to be calculated as far as the structure of a water/metal interface is concerned are the oxygen and hydrogen atom density profiles. They are shown in Figure 5 for the Pt(100) and the Hg surface. The first maxima of the O and H profiles almost coincide at distances of about 2.5 and 3.0 Å from the Pt and the Hg surface, respectively. The reduced oxygen atom densities are significantly higher than those of the hydrogen atoms. After much less pronounced second peaks in the density profiles the distributions become uniform except for statistical noise. The higher and narrower peaks near the mercury surface are a consequence of the more pronounced potential minima for this surface when compared with the Pt(100) surface (Fig. 2).

The coincidence of the positions of the first peaks indicates a strong preference for a water molecule orientation parallel to the metal surface. As a potential minimum for a single water molecule is found for an orientation where the dipole moment vector points away from the surface, this coincidence demonstrates that the water-water interactions predominantly determine the structure of even the first water layer. This is also reflected in the significantly shallower minimum for the average water-metal potential energy when compared with the potential energy for a single water molecule [4].

For the density profiles near the Pt(100) surface the excess of negative charge is indicated by shaded areas (Fig. 5). This charge distribution leads to a potential drop at the Pt(100) surface in good agreement with the measured value.

The running integration number for the oxygen atoms at the Hg surface leads to 76 water molecules in the adsorbed layer. This result shows that almost every mercury atom of the surface has a directly adsorbed water molecule.

The normalized density profiles for Li^+ and I^- together with those for the oxygen and the hydrogen atoms at the Pt(100) surface are depicted in Figure 6. The positions and the heights in the O- and H-profiles are not significantly different from those for pure water. The ion profiles show that over the whole simulation time of about 20 ps neither of the ions leaves the boundary layer.

The I^- profile extends only over the very narrow distance range $1.8 < z < 2.4$ Å. Its maximum at 2.0 Å coincides with the potential minimum for a position of the iodide ion opposite of a hollow site of the Pt(100) surface (Fig. 3). Therefore, the I^- can be called "contact adsorbed" on the Pt(100) surface, although the platinum crystal-iodide ion interaction energy is slightly less negative than the lowest potential minimum. The I^-—O first neighbour distance prevents the I^- from occupying an exact hollow site position (Fig. 7).

The density profile of Li^+ is quite different from that of I^-. In spite of the smaller size of the lithium ion the range of distances from the surface $2.0 < z < 3.2$ Å is almost completely beyond that for the iodide ion and is much broader. The maxima

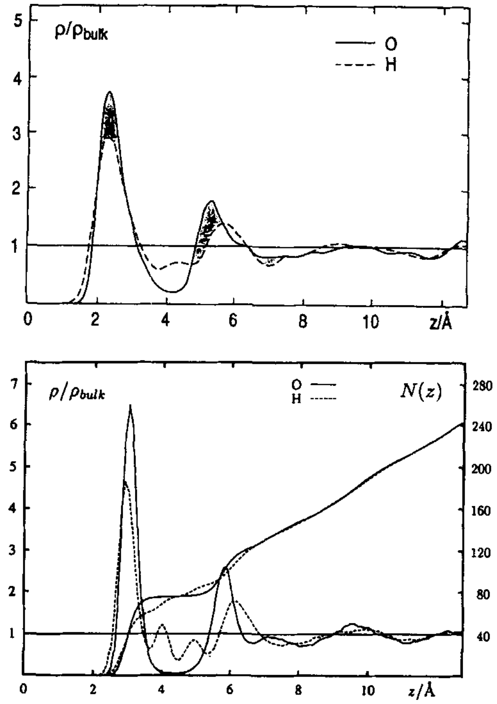

Figure 5 Normalized oxygen and hydrogen atom densities as a function of distance from the Pt(100) (top) and the mercury (bottom) surface. The shaded areas indicate an excess of negative charges, while $N(z)$ gives the number of the oxygen or half that of the hydrogen atoms in the volume between the metal surface and a distance z.

of the O- and H-atom profiles coincide with that of Li^+ at 2.5 Å. It can be seen from Figure 3 that at this distance the potential energy of Li^+ is independent of its position relative to the platinum atoms of the surface layer. It does not see a surface potential corrugation anymore. Very different from I^-, it is obvious that both the distance range of Li^+ from the surface and its position relative to the surface platinum atoms is determined by the Li^+-water and not by the Li^+-Pt crystal interactions. Therefore, it is justified to say that the Li^+ is "not contact adsorbed".

4.2 Pair Correlation Functions

The O—O, Li^+—O and I^-—O pair correlation functions, depicted in Figure 7, show that the enhancement of the hydration shell structure of Li^+ and the decrease for I^- in the surface layer results from the formation of a pronounced quadratic water overlayer with a lattice constant of the Pt(100) surface of 2.77 Å. The origin $(\Delta x = 0, \Delta y = 0)$ coincides with the changing position of an O, a Li^+ or an I^- particle in the surface layer ($z < 4.2$ Å), and $|\Delta x|$ and $|\Delta y|$ are the absolute values of the projection of the distances of the O-atoms in the surface layer from these reference particles. Both the reference particle and the O-atoms referred to, move with respect to the Pt-lattice, and the shape of the peaks results from both movements.

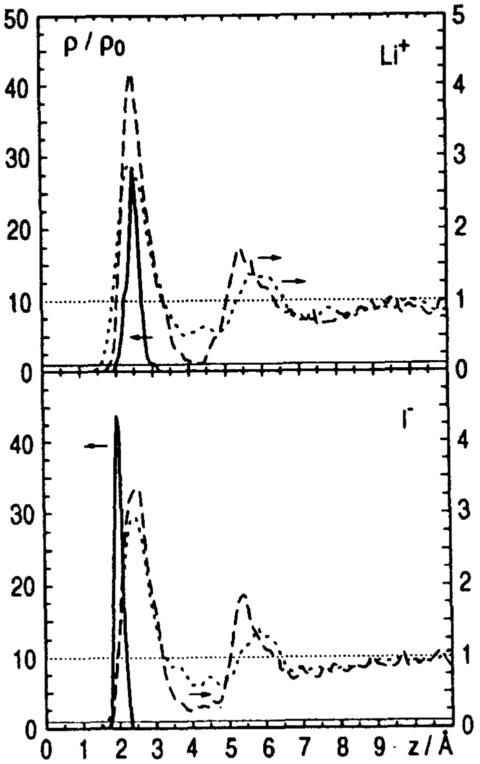

Figure 6 Normalized ion (——), oxygen (– –) and hydrogen (- - -) atom density profiles as functions of distance from the Pt(100) surface, calculated from simulations with a lithium ion (top) or an iodide ion (bottom) in the boundary layer. The arrows indicate the relevant scale.

The plot of g_{OO} reflects the positions of the oxygen atoms on the top site of the platinum lattice, and the pronounced form of the peaks refers to their relatively small displacement. The sharper peaks for g_{LiO} show that the displacements of Li^+ at its hollow site are smaller than those of O at its top, and the significantly broader ones for g_{IO} than for g_{OO} show that the displacement of I^- are much larger than those of O. Indeed the I^- moves in a relatively widespreaded area between a hollow and a bridge site.

In Figure 7 also the trajectories of Li^+ (a) and I^- (b) are drawn and the x- and y-coordinates of the oxygen atoms of the water molecules with $z < 4.2$ Å are marked by a dot after every 0.05 ps. The positions of those Pt atoms which are not covered by oxygen atoms are indicated by crosses. Over the whole simulation time of 20 ps the Li^+ remains very near to the hollow site of the Pt(100) surface at $x, y = 1$. In accordance with the pair correlation functions the distributions of the neighbouring oxygen atoms above their respective Pt atoms is very narrow. The larger I^- moves during this time in the area $-4.0 < x < -2.5$ Å and $0 < y < 1.0$ Å. It cannot occupy a hollow site as the first neighbour I^--O-distance is about 3.4 Å. In accordance with the energy curves in Figure 3 it prefers positions between a hollow and a bridge site.

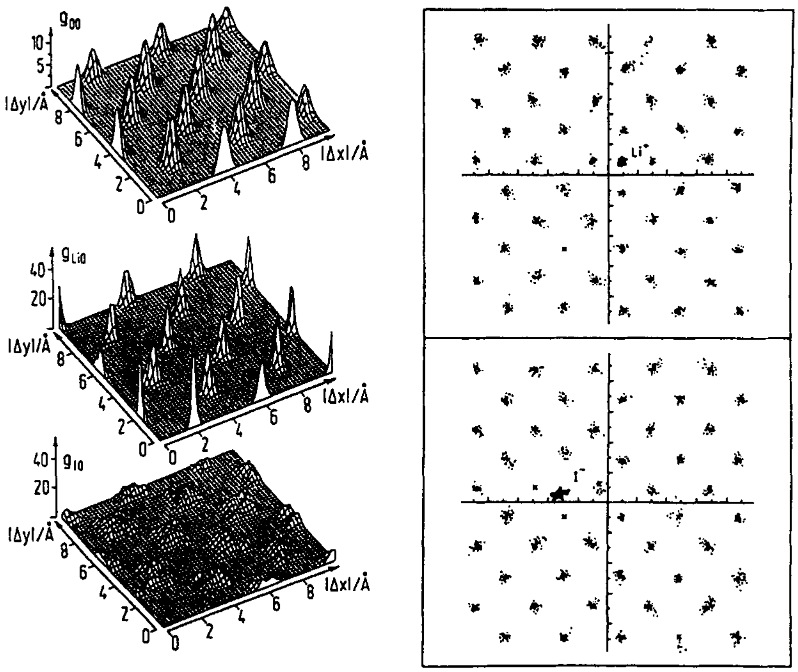

Figure 7 Oxygen-oxygen, lithium-oxygen and iodide-oxygen pair correlation functions in the adsorbed layer ($\Delta z \leqslant 4.2$ Å for all particles). Δx and Δy are the projections of the interatomic distances on the x and y directions, respectively, of the laboratory coordinate system (left). Projection of the trajectories of the lithium ions (a), iodide ions (b), and the oxygen atoms onto the xy-plane. The positions are marked by a dot every 0.05 ps. Only the oxygen atoms of the adsorbed water layer are taken into account, and the platinum atoms which are not covered with water are denoted by a cross (right).

Necessarily, two of the four neighbouring Pt atoms are not covered by oxygen atoms and their distributions around the other Pt atoms are broader than in the Li^+ case.

The geometrical arrangement of the oxygen atoms in the first hydration shells of the ions can be deduced from the simulation by the calculation of the distribution of cos ϑ, where ϑ is defined as the O-Ion-O angle. The result is depicted in Figure 8 for both ions in the boundary layer and in the bulk solution. The corresponding running integration numbers for cos ϑ are shown additionally.

The distribution of cos ϑ for Li^+ demonstrates clearly a strong preference for an octahedral symmetry in both cases. $P(\cos \vartheta)$ is narrower around 0 and -1 for the boundary layer in accordance with the well-defined nearest neighbour oxygen atom positions around Li^+ in the quadratic water overlayer (Figure 7). The hydration number of Li^+ is reduced by about one in the boundary layer. As the octahedral plane of the hydration shell of Li^+ parallel to the surface is fully occupied, the excluded volume of the surface is responsible for the missing water molecule. The fifth water molecule belongs to the second water layer and is placed on top of the ion.

It can also be seen from Figure 8 that neither in the bulk nor in the boundary layer a symmetry is recognizeable for the hydration shells of I^-. $P(\cos \vartheta)$ is practically uniform over the whole range except for the excluded volume effect for $\cos \vartheta > 0.8$ which results from the finite size of the water molecules. As the I^- is contact adsorbed the excluded volume effect of the Pt surface amounts to almost one half and is responsible for the reduction of the hydration number of I^- from 9.2 in the bulk solution to 5.1 in the boundary layer.

4.3 Hindered Translational Motions of the Ions

To investigate the hindered translational motions, the velocity autocorrelation functions (acf) are calculated from the simulations according to

$$\langle \vec{v}(0)\cdot\vec{v}(t)\rangle = \frac{1}{N_T N}\sum_{i=1}^{N_T}\sum_{j=1}^{N}\vec{v}_j(t_i)\cdot\vec{v}_j(t_i+t),$$

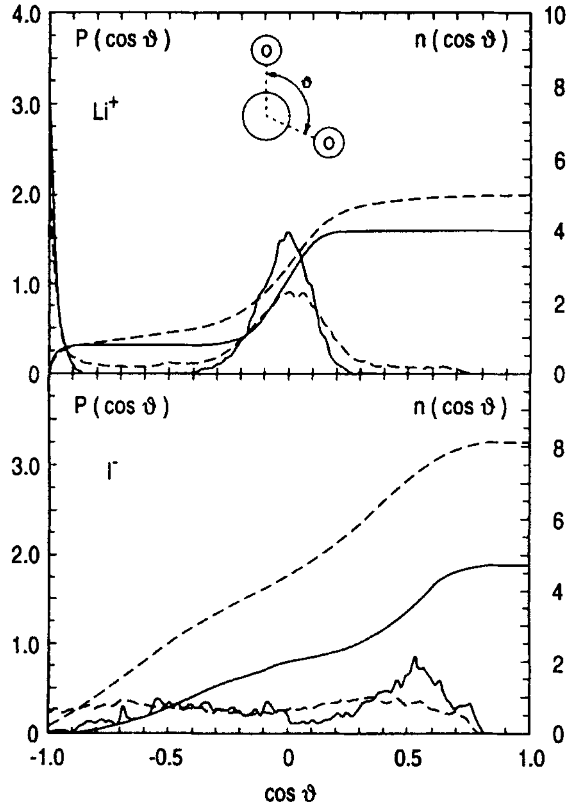

Figure 8 Distribution of $\cos \vartheta$ – where ϑ is defined in the insertion – for the water molecules in the first hydration shells of Li^+ and I^- in the boundary layer (full) and the 2.2 molal bulk solution (dashed). The corresponding running integration numbers are shown additionally.

where N denotes the number of particles, N_T the number of time averages and $\vec{v}_j(t)$ the velocity of particle j at time t. From these acfs the power spectra have been calculated by Fourier transformation.

Different from isotropic bulk systems the acfs of the particles in the lamella are functions both of the distance from the surface and the angle between the velocity vector and the normal vector. Therefore, the acfs have been calculated separately for the particles located in the boundary water layer and in the bulk region and separately for the motions parallel and perpendicular to the surface. They are depicted for Li^+ and I^- in Figure 9.

The motions of the Li^+ in the boundary layer parallel and perpendicular to the metal surface are quite different from those in the isotropic solution. The frequencies of the hindered translational motions parallel to the surface show a strong blueshift. This reflects the enhanced Li^+-water interactions as a result of the reduced water mobility, which is a consequence of the formation of the quadratic water overlayer. The motions of Li^+ perpendicular to the surface are characterized by a shift of the main peak in the spectral density to lower frequencies. This is a consequence of the greater mobility of the Li^+ because of the missing water molecule between the ion and the surface.

Different results are found in the case of the iodide ions adsorbed on the metal surface. The blue shift of the frequency maximum for the transvere motions of the ions in the boundary region is about 20 cm^{-1}. This indicates a movement of the heavy ion parallel to the surface which is only slightly disturbed by collisions with

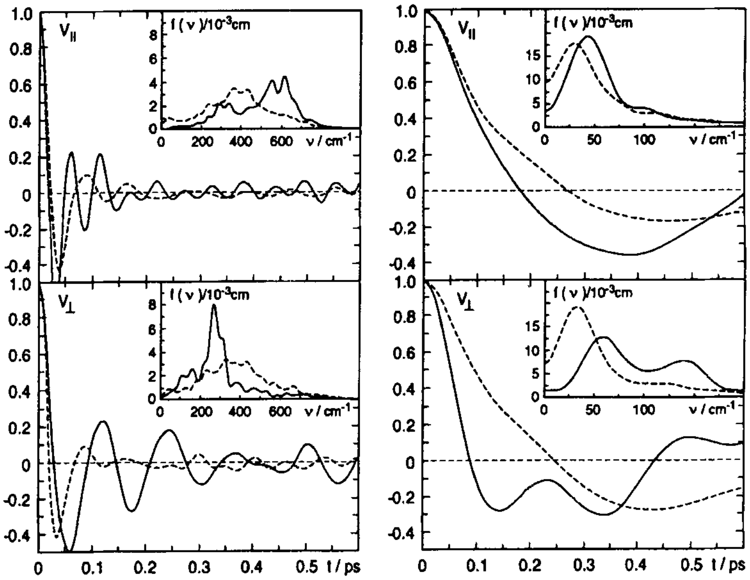

Figure 9 Normalized velocity autocorrelation functions and spectral densities of the lithium (left) and iodide ions (right) in the boundary layer (——) and the bulk (– –), calculated separately for the motions parallel (top) and perpendicular (bottom) to the Pt(100) surface.

neighbouring water molecules adsorbed at the Pt(100) surface. The perpendicular motions show a significant blue shift of the frequencies of the two main peaks, which demonstrates the strong interaction between the surface and the I^- positioned near the energy minimum.

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