Ab Initio Simulation of Metal Cluster Surrounded by Electrolyte

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An effective and computationally economical scheme, which unifies density functional description of a metal electronic structure and the classical molecular dynamics description of an electrolyte in contact with the metal, is described. The density functional part of the scheme comprises Car-Parinello and related formalisms. This scheme allows the extension to longer time scale of the simulation of metal-electrolyte interface while keeping fairly good accuracy in the prediction of the metal electronic structure. The numerical scheme is implemented in the relatively simple model of a metal cluster surrounded by an electrolyte. The elementary event of an atom leaving a metal surface as an ion stabilized by solvent molecules has been studied. In particular the potential of mean force of the ion as it dissolves was evaluated. The evolution of the solvation shell of the ion as it leaves the surface is calculated as a further example.
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Predicting the atomic scale structure of the metal-electrolyte interface is of high importance for understanding many characteristics of metal-electrolyte contacts. Molecular dynamics (MD) simulation can provide unique insight in this problem not achievable by other means. A very promising way to improve the quality of MD simulation is to combine the atomistic classical description of the electrolyte using MD based on various types of model potential approximations with density functional (DF) description of the metal electronic structure. There are several important papers aimed at developing this approach. For example, Halley, Price, and co-workers[1-4] in a series of reports have proposed some interesting implementations of combined *ab initio* and classical MD to simulate metal electrodes in water. The most challenged problem in the *ab initio* MD simulation of metal-liquid interfaces is to develop methods which allow both a relatively good accuracy in the metal electronic structure and a low computational cost that permits the extension of the simulations to a larger time scale. At the present time, all of the techniques, including the method developed by Halley, Price, and co-workers[4] only permit the simulation time up to several picoseconds. In most cases, this time is insufficient to collect reliable statistics for calculating thermodynamical data. In this report, a method of calculation which combines the *ab initio* MD of the metal electronic structure with the classical MD of the electrolyte, allows for performance of simulations of the entire system for many tens of picoseconds. To show potential advantages of the method, we have illustrated this technique with a relatively simple model to simulate some key features of physics of the metal in contact with liquid electrolyte. In particular, we have examined the metal dissolution event.

The problem of dissolution and deposition of metal in aqueous electrolytes itself is central to many electrochemical phenomena.[5-8] Besides demonstrating the ability of the method the model retains the essential physics. In particular, the model has features which allow the electron to transfer from an ion to metallic phase as the ion leaves. The model also permits the definition and subsequent exploration of issues involving the dynamics of ions leaving or arriving at the metal surface, the change in the electronic structure of the metal, and the effect of electrolyte dynamics on these processes. This note describes an *ab initio* molecular dynamics simulation of a metallic cluster in contact with an electrolyte. The implemented calculation technique is based on the Car-Parrinello *ab initio* molecular dynamics, the density functional formalism in the local density (LD), and nonlocal norm conserving Bachelet-Hamann-Schluter (BHS) pseudopotential approximations.[9-11] The water and ions comprising the electrolyte surrounding the metal are treated as objects obeying the laws of classical mechanics. It is demonstrated with this model that the simula-

tion approach developed here enables one to extend the simulation times to large time scales while keeping fairly good accuracy in the representation of the metal electronic structure. With this approach it is possible to collect reliable thermodynamic data, and study such relatively large time scale events as, for example, a formation of hydration shell. Not all issues about dissolution and deposition can be addressed by the present scheme. However the basic model can be extended, in particular by using more sophisticated potentials for water-metal electrons interaction.

Description of the Theory

Description of the model.—The basic problem is to simultaneously solve for the electronic and ionic motion in metal in the presence of a liquid electrolyte phase. Figure 1 shows the dynamical system. There are two "boxes". All the electrons of the metal cluster are con-
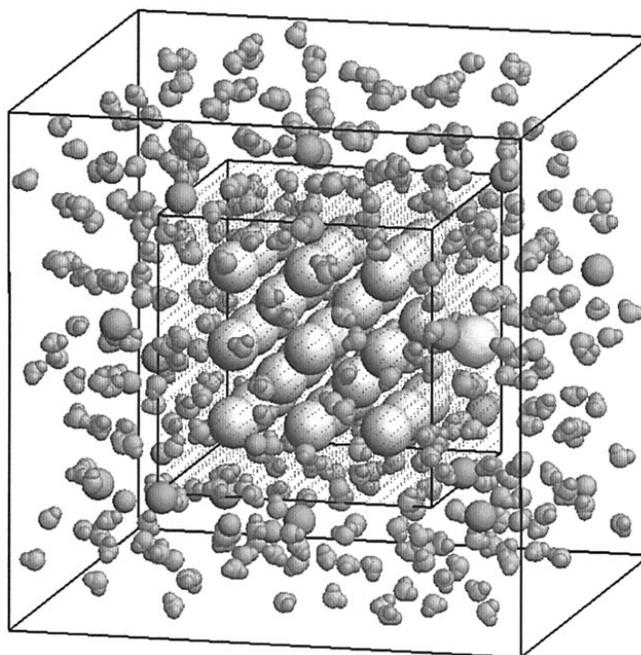
Figure 1. Snapshot of the simulation with 35 atom Li cluster. Na$^+$ small spheres, Cl$^-$ large spheres. The water molecules and lithium atoms are not to scale for clarity. The electronic charge distribution of the metal cluster is calculated inside the small box (electronic box). The large box is the classical molecular dynamics simulation cell (MD box).

fined to a cubical box of edge length L_{el} (electronic box). The cluster is surrounded by the electrolyte. The entire system is enclosed in a much larger cubical simulation box (MD box) with edge length L_{MD} and repulsive walls. We followed the Car-Parrinello scheme in the LD and BHS pseudopotential approximations to simulate the dynamics of the electronic distribution of the cluster. Only the valence electrons were treated explicitly. To extend the MD simulation to larger time scales, the Car-Parrinello dynamics for valence electronic wave functions were performed in the basis of lowest energy Kohn-Sham orbitals calculated for a reference geometry of the cluster with some specific predetermined number in the set. The reference geometry was chosen to be geometry of an ideal cluster in a vacuum. The full set of Kohn-Sham orbitals is actually a unitary transformed plane wave basis, and therefore, is complete just like the plane wave set used in their construction. It turns out in that the Kohn-Sham orbitals for a geometry different (in some small extent) from reference one can be well approximated with linear combinations of sufficiently large number of the lowest energy Kohn-Sham orbitals of the reference geometry. For convenience, we refer to this basis as a restricted Kohn-Sham basis. For relatively small perturbations the restricted Kohn-Sham basis can be chosen to be quite small. The accuracy achieved by using such an incomplete basis set can be verified independently by DF calculations in the original plane wave basis. The orbitals in the restricted Kohn-Sham basis (which comprised the basis in the Car-Parrinello simulation) were calculated once before starting the *ab initio* MD and stored in a real space representation.

In our approach the orbitals in the restricted Kohn-Sham basis had not the periodicity of the MD box which contains the whole system. Instead of using periodic boundary conditions we have expanded the orbitals into plane waves which satisfy zero boundary conditions on the edges of the electronic box. The size of the electronic box was significantly smaller than the size of the MD box. Using zero boundary conditions is reasonable because the charge density goes quickly to zero outside the cluster. To achieve good accuracy, the size of the electronic box can be chosen to ensure only that walls are in the region where the charge density is close to zero. This formalism provides good accuracy in the representation of the metal electronic structure especially in the outer region where a contact of solvent and metal charge occurs. The expansion has a form

$$\psi_i^0(r) = \sum_k \tilde{c}_i^k \, \sin(k_x r_x) \, \sin(k_y r_y) \, \sin(k_z r_z) \qquad [1]$$

where $k = (k_x, k_y, k_z)$ is a reciprocal lattice vector of the electronic box with zero boundary conditions (*i.e.*, of the form $\pi/L_{el}[m, n, p]$, where m, n, and p are integers). The smaller size of the electronic box allows us to choose a smaller size of the plane wave basis while keeping the same accuracy in the electronic structure. The Kohn-Sham orbitals are real. Note that the electronic box in this formalism could be considered as formed from walls with infinitely high potential which keep all electrons inside the volume. This interpretation enlightens another important advantage in the introducing the electronic box with zero boundary conditions. It allows for mimicking of the charge transfer from the metal ion back to the cluster as the ion becomes dissociated during simulation. The periodic boundary conditions were assumed only in order to perform the evaluations of the integrals representing the Hartree potentials using fast Fourier transform (FFT). These evaluations were done using a plane wave basis in a separate (FFT) cell which contained the original electronic box with periodic boundary conditions. To ensure that the results of such evaluations accurately represented the isolated cluster, we cutoff the Coulomb potential. The cutoff Coulomb potential minimized interaction of the charge density in the original cell with that in image cells. This enabled us to reduce the size of the FFT cell. One-electron wave functions were expanded into linear combinations of N orbitals $\psi_i^0(r)$ which comprise the restricted Kohn-Sham basis as

$$\psi_i(r) = \sum_{j=1}^N c_i^j \psi_j^0(r) \qquad [2]$$

The Car-Parinello dynamics is given by the equations

$$\mu \ddot{c}_i^j = -\frac{\partial E_{tot}}{\partial c_i^j} - \sum_{k=1}^N \lambda_{ik} \frac{\partial \sigma_{ik}}{\partial c_i^j} \qquad [3]$$

for the electronic degrees of freedom and by classical mechanics equations

$$M_I \ddot{R}_I = -\nabla_I E_{tot} \qquad [4]$$

for all nuclear degrees of freedom. Here, μ is the fictitious electronic mass, $\{M_I\}$ is the masses of the cations or atoms, and the set of parameters $\{\lambda_{ij}\}$ is the Lagrangian multipliers chosen to satisfy the following orthonormality constraints

$$\sigma_{ij} = \sum_{k=1}^N c_i^k c_j^k - \delta_{ij} = 0 \qquad [5]$$

Energy, E_{tot}, includes the interaction of ionic and electronic subsystems of the cluster with the electrolyte surroundings. We emphasize that the unperturbed basis $\{\psi_j^0(r)\}$ was calculated by conventional DF method in the plane wave basis only once before starting the Car-Parinello dynamics. The accuracy in the representation of one electron wave functions is controlled by a number, N, of orbitals included in the restricted basis. Our work suggests that for systems like the ones studied here, the size of the restricted basis can be chosen to be rather small (several times larger than number of occupied electronic states) and still achieve reasonable accuracy in the metal electronic structure. Therefore, this scheme is quite faster than some previously developed methods.

The coupled sets of Eq. 3 and 4 have been integrated simultaneously. We studied the influence of the electrolyte on many cluster properties, *e.g.*, the binding energy of the metal ion with the cluster and the charge distribution within the cluster. In particular, we calculated a potential of mean force (PMF) curve which governs the dissolution process. The other part of our simulation was concerned with the structure of solvation of metal ion during the dissolution. The evolution of solvation shell correlates well with the shape of the PMF curve. The solvation shell forms as a result of the interaction of waters with both the metal ionic core and the metal valence electrons. These calculations required us to collect statistical data for periods of several tens of picoseconds.

Details of the model.—A cubically shaped cluster of 35 one-electron atoms was surrounded by aqueous electrolyte. For computational simplicity, the atoms were taken to be Li atoms (sp-bonded metal). The Li_{35} cluster has been chosen to have the geometry of the bulk body-centered cubic crystal. However, within this geometric constraint, the bond distance, or effective lattice constant, a_{eff} of the cluster varied and the equilibrium value was obtained. The a_{eff} was found to be 6.6 au. The edge length of the electronic box was $L_{el} = 24$ au. The Car-Parrinello MD (Eq. 3, 4) of the cluster electronic structure was performed in the restricted Kohn-Sham basis $\{\psi_j^0(r)\}$ with a predetermined number of orbitals in the set. These orbitals were calculated for the Li_{35} cluster in vacuum in plane waves with 20 Ry kinetic energy cutoff which is reasonable for sp-bonded metal. The Hartree integrals were evaluated using expansion of charge density in plane waves in separate supercells with an energy cutoff about 60 Ry. The number N of orbitals in the restricted Kohn-Sham basis was chosen to be $2 \times M$, where M is a number of occupied Kohn-Sham states (see Eq. 2). The number N is the smallest number of basis functions to make it possible to satisfy the $(\psi_i, \dot{\psi}_j) = 0$ constraint which is compulsory for the Car-Parrinello part of dynamics. As is shown, this number is sufficient to achieve a good accuracy in the prediction of the electronic structure of the Li_{35} cluster with one surface ion going into solution.

We have studied the dynamics of a single centrally located ion on the (001) surface with all other cluster ions at fixed sites. To speed up calculations, the projection part of the BHS pseudopotential for the moving ion was tabulated on a fine grid along normal direction

to the cluster surface. The ion was allowed to move only in that direction. The electrolyte was 1.65 M aqueous NaCl solution and represented by a collection of 800 water molecules, 24 sodium ions, and 24 chloride ions. The assembly was maintained using a cubic confining potential of the MD box that reflected waters and ions attempting to evaporate from the assembly. With such an assembly of the electrolyte, we avoided the complications involved with periodic boundary conditions and techniques to account for sums of long ranged electrostatic interaction.

In this paper, a cube-shaped cluster of 35 one-electron atoms was surrounded by a collection of water molecules [modeled by the simple point charge (SPC)/E model of Berendsen[12]], and simple ions (modeled as charged Lennard-Jones soft spheres). For computational simplicity, the potential parameter for ion-water and water-water interactions were taken from Ref. 13 and 14. The edge length of the MD box was $L_{MD} = 55.53$ au. The well known named algorithms of molecular dynamics were used to determine the trajectories. For example, integration of the equations of motion for ionic and valence charge density of the cluster was performed using Verlet's algorithm. The orthonormality constraints (see Eq. 5) on the one-electron wave functions were implemented using the energy conserving Shake algorithm.[15] The equations of motion of the constituents of the electrolyte were integrated using the combined Verlet and Rattle algorithms.[16] This was done to keep the bonds and angles fixed for the SPC/E water molecules. The equations of the system were integrated in multiscale MD fashion. The equations of motion for the electrolyte were integrated with a time step 1.0 fs, while the equations for charge density and metal ion motions were integrated with a time step 0.25 fs. The constant temperature around 300 K was maintained using an Anderson thermostat.[17]

An elementary act of dissolution in our model could be considered as a transfer of metal ion from the cluster to the electrolyte. This was facilitated by rearrangements of the electrolyte dipoles and charges. Only "physics" was permitted in our model. There was no chemistry between electrolyte and metal cluster. The interaction of the water with the metal valence electrons was composed of two parts. The first was a purely long-ranged electrostatic term that was taken to be that produced by the charge distribution of the SPC/E model. The second term was a spherically symmetric polarization term, centered on the oxygen nucleus, taken from molecular scattering theory.[18] This interaction is short-ranged. The Na^+ and Cl^- ions interacted with the metal charge by electrostatic interaction only. This model did not explicitly include a term for Pauli repulsion in the interaction of the metal charge with the electrolyte species. This repulsion to some extent was mimicked by the repulsion part of potential between water molecules and metal ions which is described below. The interaction between metal ions and electrolyte ions was described by a pair potential of the Born-Mayer-Huggins type. A difficult question was the proper choice of water-lithium ion short-ranged interaction for lithium in the solvent and inside the cluster. We have taken this short-ranged interaction to be of the Lennard-Jones (6,12) type. This potential seems to be good enough to reproduce realistically the development of the solvation shell as the Li^+ ion leaves the cluster and enters the electrolyte phase. The adaptation of the interactions developed in this model is useful for clarifying the role of the electrolyte in the dissolution of metal due to the polarization effects. In the Car-Parinello scheme, the wave functions and therefore the charge density, are correct only after the relaxation of charge density to the ground state. However, if the time of relaxation of charge density to the ground state is small compared to the characteristic time of motion of metal ion and electrolyte species, the Car-Parinello scheme can reproduce the correct dynamics of the charge density. The fictitious electronic mass was 3,000 au. This corresponds to a relaxation time of roughly 10 fs for the charge density.

An Atom in the (001) Surface of an M_{35} Cube

Some structural and dynamical properties of the Li_{35} cluster in a vacuum are presented as calculated in the simulation to demonstrate the quality of our approach in treatment of the metal electronic struc-

ture. The errors in the simulation of the cluster electronic structure could arise from approximations either by introducing the electronic box with zero boundary conditions or by using the restricted Kohn-Sham basis. To ensure that zero boundary conditions imposed by the electronic box with chosen size did not affect the electronic structure properties of the cluster in the simulations, the DF calculations were conducted in plane waves for the cluster in vacuum using electronic boxes of different sizes. The binding energy of the cluster per atom calculated for the electronic box with edge length of 24 au was 1.23 eV. This value is consistent with the existing literature data.[19] The increase in the size of the electronic box did not affect the calculated value of the binding energy if the same cutoff for kinetic energy was applied. This indicates that the chosen size of the electronic box is suitable for the simulation in the sense that walls of the electronic box fall in the region of zero charge density. The central ion on a (001) cluster surface for which we have studied dynamics, was bonded to the cluster with energy of 7.34 eV as was obtained by DF calculations in plane waves. The binding energy for the same atom was 2.11 eV. These energies yield a cluster affinity of ~0.2 eV. It is in reasonable agreement with jellium calculations in linear density approximation.[20] These calculations suggested that for the size of the cluster we studied, the affinity is significantly smaller than the work function. To clarify the effect of an incompleteness of the restricted Kohn-Sham basis on the metal structure calculations, an *ab initio* MD simulation of the cluster in vacuum was performed. In particular, the total valence electronic energy (actually the free energy) of the cluster in vacuum was calculated as a function of distance of the ion to the equilibrium position in the cluster. The resulting curve is plotted in Fig. 2. This curve was calculated by fixing the ion cluster separation and integrating the Car-Parrinello equations of motion for electronic degrees of freedom (Eq. 3) until the charge density was fully relaxed. To estimate the accuracy achieved by using the Car-Parrinello simulation in the restricted Kohn-Sham, the ion cluster binding energy obtained by *ab initio* MD was compared with the results of DF calculations. *Ab initio* MD yielded 7.40 eV (this value cannot be readily estimated from the portion of the total energy curve presented in Fig. 2 because only the small separations are shown). This is in close agreement with the value of 7.34 eV obtained in plane waves calculations. The calculated frequency of oscillations was approximately 92 fs (365 cm^{-1}). The equilibrium position of the ion during the oscillations shifted slightly (~0.7 au) inside the cluster that was obvious due to the fact that the cluster geometry is not fully optimized.

The solvation energy of Li^+ ion in bulk SPC/E water is about −9.45 eV [14] and is compared with a depth of the potential well for the Li^+ ion in the cluster that is around −11.0 eV. The latter energy is equal to the binding energy of the ion to the cluster minus a change in the valence electronic energy of the cluster as the ion is removed. Thus, the system can exhibit a free energy barrier to a dissociation of the Li^+ ion in pure water. We evaluated the change in the free energy as the metal ion dissolves by a calculation of the PMF curve for the

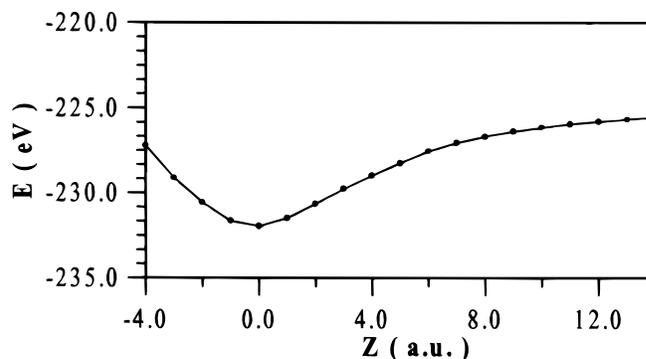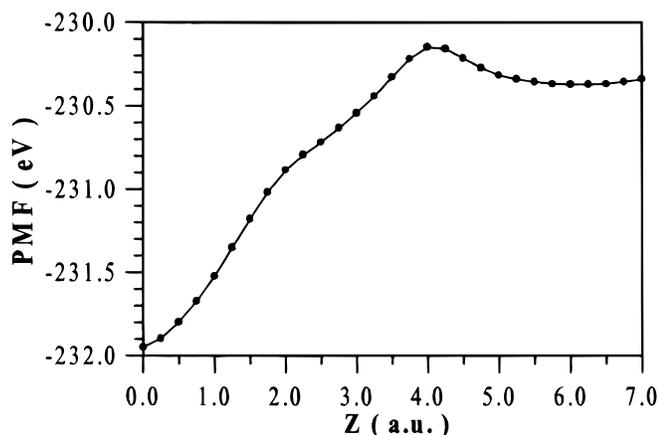**Figure 2.** The total energy, *E*, of the cluster *vs.* the distance, *Z*, of the ion to the equilibrium position in the cluster.

metal ion along a reaction coordinate. In our model, the reaction coordinate was assumed to be the distance of the ion to the equilibrium position in the cluster. The reaction coordinate, which is actually an axis normal to the cluster surface, is a linear function of the configuration degrees of freedom. In this case, the PMF can be calculated by fixing the metal ion on the specific distance from the cluster and calculating a mean force acting on the ion in the direction normal to the cluster surface.[21] The average force has to be subsequently integrated to produce PMF dependence. For the present calculations the ion was fixed at distances ranging from 0.0 to 7.0 au from the cluster. Within this range, a first peak in the PMF curve was observed to be fully developed. The simultaneous integration of equations of motion for the electrolyte and the metal electronic structure is still computationally expensive for the PMF curve with small step. To speed calculations, the averaging scheme for each fixed position of the Li^+ ion was chosen as follows. The electrolyte was integrated for 0.1 ps at the frozen electronic structure followed by 0.05 ps of charge relaxation at the frozen electrolyte configuration. We checked the reliability of this averaging scheme by performing simultaneous simulations of the electrolyte and the metal electronic structure at several selected points in the barrier regions of the PMF curve. The agreement was satisfactory. The total simulation time at each point of separation was around 10 ps and was preceded by a 30 ps equilibration period for the electrolyte at the frozen configuration of the metal charge. We have done these calculations starting with an initial electrolyte configuration prepared to avoid association of Li^+ and Cl^- ions. The PMF curve is shown in Fig. 3. The distance 0.0 au corresponds to the equilibrium position of the metal ion in the cluster in vacuum. The PMF exhibits well defined barrier. This barrier is located at 4.0 au from the cluster, and separates the chemisorbed state in the cluster and the dissociated state where the ion is surrounded by the solvent. As is discussed later, the metal ion was strongly solvated at this distance. The barrier is followed by the minimum which corresponds to the physically absorbed state. The height of the barrier to the physically absorbed state is 1.80 eV. The physically absorbed state exhibits barrier of 0.22 eV in height to the chemisorbed state. The chemically and physically absorbed states are similar to the contact ion pair and the solvent separated ion pair in electrolyte systems. The barrier, which separates the states of the metal ion in the cluster and in the electrolyte, is high. That means that the neutral cluster would not dissolve at room temperature when surrounded by the small pocket of electrolyte considered in the model described here. This could be remedied in three ways: (*i*) with a larger embedding electrolyte cluster so that the full dielectric response of the electrolyte could develop, (*ii*) by applying an external electric field to mimic potentiostatic tuning of the electrode, and (*iii*) by repeating the calculations with charged clusters.

We made preliminary estimations of the effect of ion pair formation of the Li^+ ion with negatively charged ion on the height of the barrier to the dissociated state. In this set of calculations, the Cl^- ion was placed on top of the Li^+ ion and was allowed to move freely along the z axis (direction normal to the cluster surface). The PMF curve was calculated by pulling slowly the Li^+ ion in the direction normal to the cluster surface starting with the equilibrium position,
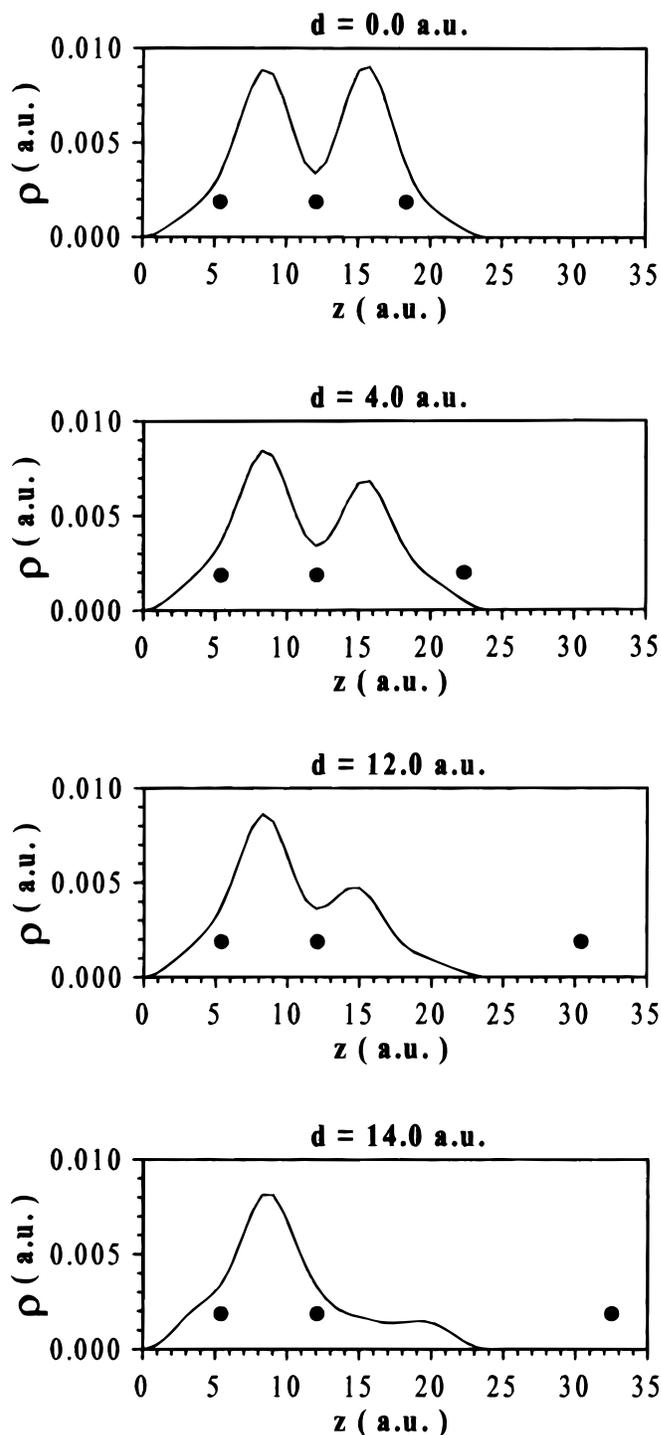
Figure 4. Time average of the change in the electronic density, ρ, with increasing separation, *d*, of the metal ion from the cluster. One-electron wave functions are represented as linear combinations of the lowest Kohn-Sham orbitals obtained for undistorted geometry of the Li_{35} cluster in vacuum. The charge density is zero beyond the distance of 24.0 au as a result of zero boundary conditions for Kohn-Sham orbitals basis set.

Figure 3. The ion-metal cluster PMF *vs*. distance, *Z*, of the ion to the equilibrium position in the cluster. The free energy of the system for a distance of 0.0 au was set to that of the cubic cluster in vacuum (see Fig. 2).

while the force acting on the Li$^+$ ion was integrated. The Li$^+$ ion was pulled with a velocity of 1 au per ps until maximum in the PMF curve was reached. The shape of the obtained PMF curve was similar to the shape of the PMF curve presented in Fig. 3. However, although the barrier was lower by about 0.15 eV, it was still too high for high metal dissolution without applying positive potential. We also observed that a minimum in the PMF curve corresponding to the chemisorbed state was much shallower than the one in the PMF curve calculated in the absence of the Li$^+$-Cl$^-$ complexation.

Figure 4 shows time averaged charge density profiles along the direction through bulk cluster atom for different ion cluster separations. The time for the data collection was 20 ps for each separation. The simultaneous dynamics of the metal charge and the solvent surrounding was simulated. Note a hole in the charge distribution of the cluster forms for the ion cluster separations in the range of approximately 12-14 au, which is much larger than the average distance between the cluster and the Li$^+$ ion in the physically absorbed state (see Fig. 3). In Fig. 4, due to the zero boundary constraints, the charge is zero beyond a distance of 24.0 au.

A comparison of features in the shape of the PMF curve with dynamics of development of the solvation shell as the Li$^+$ ion goes into solution is shown in Fig. 5. The radial distribution function $g(r)$ and the hydration number $n(r)$ [integral of $g(r)$] were calculated for the ion fixed at different distances d = 0.0, 4.0, and 8.0 au from the cluster surface. These radial distribution functions have a large error bar because of a limited time of data collection, the geometry of the system, and the presence of freely moving solute ions. However, the first peak of the radial distribution function is usually formed in first 5 ps of simulation time. When the ion was in the equilibrium position in the cluster, the first hydration shell was formed from one molecule which was on top of the ion. The first change in the slope of the PMF curve which occurred at 2.0 au was due to the Lennard-Jones interaction of the Li$^+$ ion with the water molecule on the top site. During the transition to the physically absorbed state, the hydration shell was formed from four water molecules which should be regarded as complete. At the separation d = 8.0 au, the hydration shell contained four (occasionally five) water molecules. Because a second peak in the radial distribution function is fully developed and its position (7.8 au) is consistent with a bulklike environment,[14] we can conclude that the Li$^+$ ion experiences bulk water at this separation.

Conclusions

Combined *ab initio* and classical MD approaches are powerful tools for the investigation of metals in contact with liquids. The high computational cost of simulation of the metal electronic structure dynamics has remained a major obstacle in performing large time scale simulations of the metal-electrolyte contact. The proposed scheme for *ab initio* MD simulation of evolution of the metal electronic structure based on the Car-Parrinello method in density functional formalism provided a fairly good accuracy at a comparatively low computing cost. The low computational effort in simulation of the electronic structure achieved in our approach opens the possibility for extending the simulation time scale significantly. The technique was applied to reveal the role played by the electrolyte in the dissolution process. A simple model of a metal cluster surrounded by an electrolyte was chosen to investigate this phenomenon. The elementary act of dissolution in our model could be seen as a transfer of the metal ion from the cluster ion the electrolyte permitted by concomitant rearrangements in the electrolyte; the preliminary free energy calculations showed that this is a possibility. The PMF dependence manifests a well-defined reproducible maximum. This maximum is associated with the transition state of the system which separates the chemically and physically absorbed states of the metal ion. However, the barrier is rather high to expect dissolution of the metal at room temperatures without applying a potential.

The developed approach seems to be very promising. It could be easily extended to the periodic systems like infinite metal slabs in contact with an electrolyte. Another possible area of applications of

our technique that goes beyond the metal-electrolyte interface could be its use to study dissociation of single molecules like alkali halides in polar solvents because the change in the electronic structure of ion pair is small.
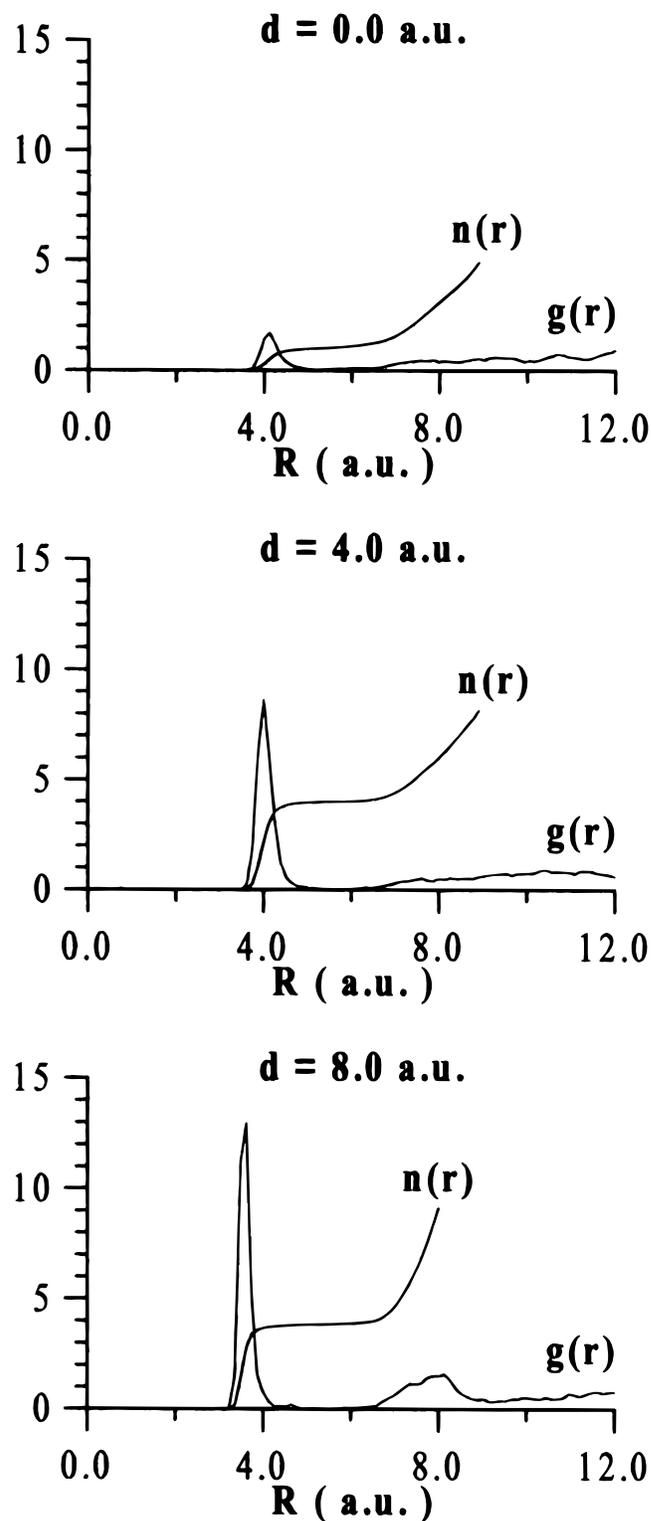
Figure 5. Radial distribution function $g(r)$ and corresponding running integration number $n(r)$ for the Li$^+$ ion separated by a distance, d, from the cluster: (top) d = 0.0 au metal ion in the surface (001) plane, one water molecule in the solvation shell; (middle) d = 4.0 au metal ion has four water molecules in the first solvaton shell; (bottom) d = 8.0 au the radial distribution function has a bulklike shape. The metal ion has four water molecules in the solvation shell.

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