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1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE November 1993	3. REPORT TYPE AND DATES COVERED Technical Report 7/1/93-6/30/94

4. TITLE AND SUBTITLE

Free Energy Profiles for Li^+ and I^- Ions Approaching Pt(100) Surface: A Molecular Dynamics Study

5. FUNDING NUMBERS

Grant N00014-89-J-1169
RT 4131036

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report #14

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000
(Code 1113PS, P.P. Schmidt)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

DTIC
ELECTE
DEC 06 1993
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11. SUPPLEMENTARY NOTES

Journal of Physical Chemistry, in press

12a. DISTRIBUTION/AVAILABILITY STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

SEE ATTACHED ABSTRACT.

14. SUBJECT TERMS

Potential of mean force, aqueous solutions at the interface with the metal

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT

OFFICE OF NAVAL RESEARCH

Grant N00014-89-J-1169

R&T Code 4131036

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by

L. Perera and Max L. Berkowitz

Journal of Physical Chemistry, in press.

The University of North Carolina at Chapel Hill
Department of Chemistry
Chapel Hill, NC 27599-3290

NOVEMBER 1993

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FREE ENERGY PROFILES FOR Li^+ and I^- IONS APPROACHING Pt(100) SURFACE: A MOLECULAR DYNAMICS STUDY.

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Abstract

We calculated the potential of mean force profiles for Li^+ and I^- ions approaching non-charged Pt(100) surface and solvated in water. These profiles show that while for I^- the traditional picture placing the anion in contact with the metal surface is justified, for Li^+ the traditional picture presenting the cation separated from the metal surface by layers of water is not correct.

Introduction.

The understanding of structural and dynamical properties of electrolytes next to the metal surface is of primary importance to electrochemistry. While the detailed molecular description of the electrolyte/metal interface is still hard to obtain from experiment [1], computer simulations seem to provide us with such a description [2-19]. Thus for example, recent molecular dynamics computer simulations on water/Pt interface produced a rather detailed picture of the structure and dynamics of water at this interface [6-13]. It is now quite obvious that the next step in the investigation of this interface is to study the effects due to the addition of ions to the interface. And indeed this was done recently by Rose and Benjamin in the study of the solvation of Na^+ and Cl^- at the water/Pt(100) interface [16]. Very recently Spohr considered the solvation of I^- ion at the same interface [18].

One of the important questions that computer simulations can help in answering is what is the most stable configuration that ions achieve at the interface? The traditional picture is the one where a large anion loses its water solvation shell and comes in contact with the metal surface, while a small cation preserves its solvation shell and therefore does not come in close contact with the metal, is this picture correct? To answer this question one should calculate the probability p(r) of finding the ion at distance r from the surface plane, or one can calculate the potential of mean force (pmf) between the surface and the ion, W(r), which is directly connected to the probability p(r) by a simple relationship:

$$W(r) = -kT \ln p(r) \tag{1}$$

In equation (1) k is the Boltzmann constant and T is the temperature of the system. In this paper we present the results from our calculations on the pmf between I^- ion solvated in water and Pt(100) surface, and the pmf between Li^+ solvated in water and Pt(100) surface. The two particular ions were chosen because they represent the extremes in their sizes and therefore are well suited for testing the classical picture. In addition the gas phase potentials of interaction between these ions and the Pt surface are available in the literature [20].

Methodology.

Our molecular dynamics simulation was performed using a rectangular box (1.96*1.96*4.22nm) which contained 512 water molecules placed between two parallel platinum slabs that had their (100) surfaces directly exposed to water. The separation distance between the two layers of Pt centers directly touching water molecules (4.22 nm) was selected so that the density of water in the middle of the box was about $1 g/cm^3$. Both ions were placed in one simulation box and even at their closest separation (~2.0 nm), we assumed that there is no direct interaction between the two ions.

The SPC/E model [21] was implemented to represent the water-water interaction, while the ion-Pt interaction was taken from the work of Seitz-Beywl et. al [19,20]. The ion-water interaction was represented by a Lennard-Jones plus Coulomb terms, i.e. we used the following form for this interaction:

$$U_{wi} = (A/r^{12} - C/r^{6}) + \sum_{j} q_i q_j / r_{ij} \qquad (2)$$

In equation (2) r is the distance between the ion center and the oxygen site on the water, q_i the charge of the ion, q_j is the charge on the site j of water molecule, r_{ij} is the distance between the ion center and the site j of the water. The values of the parameters (A and C) for the ion-water Lennard-Jones interaction are $A = 18927$ Å^{12}kJ/mol, $C = 313.2$ Å^{6}kJ/mol for the Li^+ ion and $A = 37628358$ Å^{12}kJ/mol, $C = 12140.4$ Å^{6}kJ/mol for the I^- ion. These parameters were obtained by a fit to the potential representing the ion-water interaction that was published in the literature [19]. To save a significant amount of computer time we represented the water-metal interaction in the same form as that used by us previously [11-13]. This form allowed us to concentrate on the motion of water molecules only, replacing all the Pt atoms by an effective field. The symmetry of the surface and its corrugation were also taken into account by the effective potential. However, the surfaces were given their complete atomic description when the ion-metal interaction was computed. To calculate these interactions we considered nine layers of Pt atoms which were kept at fixed positions during the molecular dynamics runs. Therefore we had to compute only once the ion-surface interaction for a given position of the ion. We made certain that the positions of the surface boundaries coincided for the water-surface and ion-surface interactions.

The equations of motion were solved using Verlet algorithm [22] and the water molecules were constrained to their geometries by implementing the Shake procedure [23]. Periodic boundary conditions were applied in the directions parallel to the interface. We used a spherical cut-off scheme in our molecular dynamics simulations, with all interactions truncated at 0.92 nm (a smoothing of the potential over the last 0.04 nm was applied). Corrections for the long range interactions were neglected beyond the cut-off distance.

To calculate the potential of mean force we first calculated the mean force acting on the constrained ion and subsequently integrated this force. In general, due to the corrugation of the surface the mean force depends on the position of the ion in the plane parallel to the surface (x,y plane) and also on the distance from the surface (z-coordinate). A complete exploration of such a force is too complicated and we therefore restricted ourselves to the study of the potential of mean force when x and y coordinates were fixed, so that the ion was always located on a line perpendicular to the surface and crossing through the hollow site of the Pt surface. Heavy masses were assigned to the ions in order to constraint them at the desired positions. Initially the ions were placed in the middle region of the box, each about 1.02 nm away from the corresponding surface. Once the positions were selected, the system was equilibrated for 5 ps with a 2.0 fs time step. The mean force acting on the ion was calculated after subsequent 26 ps of the production run. To move the ions to their new positions, the heavy masses were removed and an external forces were applied along the required directions to allow the system to evolve for 1-2 ps, until the ions came to the new positions closer to the walls. The average temperature of the system was kept around 300 K by occasional rescaling of the velocities of the particles in the system. The average force was checked to be close to zero (within the statistical accuracy) in x and y directions. Potentials of mean force along z-direction were evaluated from the integration of the mean forces calculated at 33 different points along the line described above. This method is basically the same as that used by Spohr in his recent calculation of the pmf for the I^-/Pt(100) surface [18]. Note that in our simulation we are able to get two pmf's simultaneously and observe that the system is also electroneutral in our simulation.

Results and Discussions.

From the outset we should make it very clear that our results depend on the quality of the potentials used in the simulations. Among the four potentials that we need for our simulations (water-water, water-surface, water-ion and ion-surface potentials) the best known to us are water-water potentials, since a large number of investigations and papers were devoted to this subject [24]. The water-ion potentials are also considered to be known rather well, (for some ions better than for others) although many unresolved questions and discrepancies between the experimental data and simulations still exist [25,26]. The least known are the water-surface and especially the ion-surface potentials. Due to the size of the problem, the calculation of these potentials using ab-initio methods is a very difficult task [27-29]. Therefore the potentials we use to represent the ion-surface and water-surface interactions were deduced from the calculations done on the water-small Pt cluster [30] and ion-small Pt cluster [20] complexes. Presumably these potentials describe more accurately the region close to the surface, while the region further away from the surface may be appropriately described by the image-charge model. It is possible to construct a potential for the ion-surface interaction, which will behave as the one from quantum calculations when the ion is close to the surface and will have a tail as if the interaction is due to the image-charges. But since the location of the image plane is not known and since we are interested in the behavior of the ions close to the surfaces we decided to use the same potentials as used before in the simulations by Spohr [18] and Seitz-Beywl et.al. [19].

To calculate the pmf's we first calculated the mean forces acting on the ions. These are displayed in Figures 1 and 2 for I^- and Li^+ respectively. The pmf's, which are obtained through the integration of the mean forces are displayed in Figures 3 and 4. To understand the effect that the solvent has on the mean force and the pmf, we display the corresponding contributions of the ion-surface force and the mean force due to the water.

Comparison of Figures 1 and 3 with the corresponding figures from the work of Spohr [18] shows that our pmf for I^- and his are in good agreement. The pmf for I^-/Pt(100) in water displays two minima: a deep one situated 0.2 nm away from the metal surface and another shallow one at 0.6 nm away from the surface. The shallow minimum is separated from the deep minimum by a barrier of ~9 kT (the value of barrier in ref.[18] is ~3kT). To find out where with respect to the water layers the extrema in pmf are located we display in Figure 5 the densities of oxygen and hydrogen of water embedded between two Pt(100) walls. As we can see from Figures 1,3 and 5 the most probable position of I^- is in contact with the Pt(100) surface; at this position the ion is even closer to the Pt surface than the first water layer. This is not surprising, considering that I^- displays a strong attraction towards the hollow site on Pt(100) surface (the minimum of the gas phase I^-/Pt(100) potential is found for a hollow site configuration [20]). The second minimum in the I^-/Pt(100) pmf is located around the position where the second water layer is observed, while the barrier peak in pmf is located right between the first two water layers. While the global minimum in pmf is due to the interaction between the ion and the wall the second minimum and the barrier are mostly due to the water-ion interaction. The barrier in the pmf exists because a large distortion in the structure of the water has to be created prior to penetration of a large ion such as I^- towards the surface. This is confirmed by observation of trajectories of water molecules that belong to the layer adjacent to the wall. Figure 6 displays such trajectories of waters, conditional that I^- ion is located at the top of the barrier of the pmf. As we can see from this figure a large restructuring of the water layer adsorbed to the surface have occurred at this point. The water molecules that are adsorbed on the surface prefer to sit on the top of the Pt atoms, but as we can see from the Figure 6, to adjust to the presence of the ion they moved to the interstitial positions. Even when the ion is in contact with the Pt surface, its surrounding water molecules are still not in their a-top positions due to the large size of the ion. This is illustrated in Figure 7.

The shape of the pmf for I^- that predicts a contact adsorption of the ion to the Pt surface is in agreement with the traditional picture, while the pmf for Li^+ ion presents a picture that is in disaccord with the traditional description. According to this description a small ion such as Li^+ should keep its solvation shell around itself and be separated from the metal surface by roughly two water layers, one due to its own shell and another due to the adsorption to the metal surface water layer. As Figures 2 and 4 show the most probable location of Li^+ ion is not far from the surface, i.e. 0.21 nm away from it. At the same time this is not a case of a contact adsorption, since the contact adsorption for Li^+ would occur at 0.1 nm as the surface-ion potential shows [20]. The location and the value of the minimum in the pmf for Li^+ is the result of the interplay between the ion-surface and the ion-water interactions. Because the ion experiences a large attraction towards the surface (its value is 265 kJ/mol [20]) it wants to be attached to the surface. But since it wants to keep its solvation shell because of a strong ion-water interaction it can not come into close contact with the wall. As a result the ion finds itself in a slightly elevated position from the surface and is surrounded by four nearest water molecules, which are sitting in an a-top positions of the Pt surface. The compromise state is also due to the fact that the small size of Li^+ ion allows it to sit on the hollow adsorption site without disturbing the water neighbors that attach to the a-top sites. This picture is confirmed by the display (see Figure 8) of the trajectories of water molecules that belong to the adsorbed layer.

As Figure 4 shows the pmf for the Li^+ ion also displays a barrier when the ion is located between the first and the second water layers. And again this barrier is due mainly to the water-ion interaction. At this location the ion experiences a large repulsive force from the hydrogens of the first water layer that try to prevent the ion from penetration to this layer.

To see if the first solvation layer of water around Li^+ undergoes restructuring as the position of the ion with respect to the metal surface changes, we plotted the coordination number as a function of distance to the wall in Figure 9. For the distances far away from the surface we observe a coordination number around the Li^+ ion of 4 in our simulation. This coordination number was also observed by us in an independent simulation of Li^+ ion solvated in bulk SPC/E water. The coordination number of 4 from our simulation is different from the often-reported coordination number of 6, obtained in many computer simulations for the Li^+ ion in bulk [25,26]. But it seems that most of the experimental studies by X-ray and neutron scattering from electrolyte solutions predict that the coordination number for Li^+ is actually 4 [25,26]. At the larger distances away from the surface we observed four water molecules in a tetrahedral environment around the Li^+ ion. When the ion started to penetrate the first layer the coordination number increased to 5; four waters in plane with the ion and one on top of the ion. The coordination number returned to the value of 4 when the ion was close to the wall, only at this time four water molecules were in the same plane with the ion. To get a better feeling of the geometry of water/ion/surface complex when the ion is next to the surface, we display the snapshots of typical configurations in Figures 10 and 11.

Conclusions.

We performed molecular dynamics computer simulations to calculate the potential of mean force for the I^- and Li^+ ions solvated in water and approaching the Pt (100) uncharged surface. The shape of pmf predicts a contact adsorption of I^- ion at the surface. For the Li^+ ion although a contact adsorption is not observed, the most probable location of the ion is much closer to the surface than predicted by the traditional picture of electrolyte solutions. The close proximity of the Li^+ ion to the Pt surface is not only due to the large ion-surface interaction, but is also a consequence of the small size of the ion and the fact that its adsorption site is the hollow site, while water adsorbs at the a-top position. Our calculations also show that to achieve their most stable positions close to the wall, both ions have to overcome a free energy barrier; for Li^+ this barrier is larger than for I^-. This will have its implications on the dynamics and kinetics of the ionic motion in electrolytes at interfaces.

As we have already mentioned the detailed shape of the pmf may be a function of the potentials used in the simulations, but the qualitative features of the results are in agreement with the previous simulations on electrolyte solutions at metal surfaces [14-19].

Acknowledgements:

This work was supported by a grant from the Office of Naval Research. The simulations were performed on the Cray YMP at the North Carolina Supercomputing Center and on Convex C240 at UNC.

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Figure Captions:

Fig. 1. The mean force on the I^- ion due to water molecules, the force from the surface and the total mean force (sum of the first two quantities) as a function of the distance between the ion and the Pt(100) surface.

Fig. 2. The mean force on the Li^+ ion due to water molecules, the force from the surface and the total mean force (sum of the first two quantities) as a function of the distance between the ion and the Pt(100) surface.

Fig. 3. The potential of mean force and its components, calculated for the I^- ion, as a function of the distance to the ion from the surface.

Fig. 4. Same as in Fig. 3, but for the Li^+ ion.

Fig. 5. Atomic density profiles (solid line for oxygen and dotted line for hydrogen). The I^- ion was moving towards the left wall (located at -2.11 nm) and the Li^+ ion was moving towards the right wall (at 2.11 nm). The global minima of the potentials of mean force are marked by (◆) and the maxima by (x). Also, the second minimum for I^- is marked (▲).

Fig. 6. XY projection of the trajectories of water molecules adjacent to the wall from a 26 ps simulation in which the I^- ion is in the top of the barrier of the potential of mean force. The ion projection is at (0,0) and it is marked by a cross.

Fig. 7. XY projection of the trajectories of the molecules adjacent to the wall from a 26 ps simulation in which the I^- ion is in the global minimum of the potential of mean force. The ion projection is at (0,0) and is marked by a cross.

Fig. 8. Same as in Fig. 7, but for the Li^+ ion.

Fig. 9. The coordination number of Li^+ as a function of the distance to the wall.

Fig. 10. A snapshot of a typical configuration from the I^-/Pt/water system. Not all of the adsorbed water molecules are shown for clarity. The water molecules in the solvation shell of the ion can be seen to be slightly above the rest of adsorbed water molecules.

Fig. 11. A snapshot of a typical configuration from the Li^+/Pt/water system. The ion is seen slightly below the first adsorbed water layer (some of the water molecules including one from the coordination shell of the ion were removed for clarity).

Fig. 1.

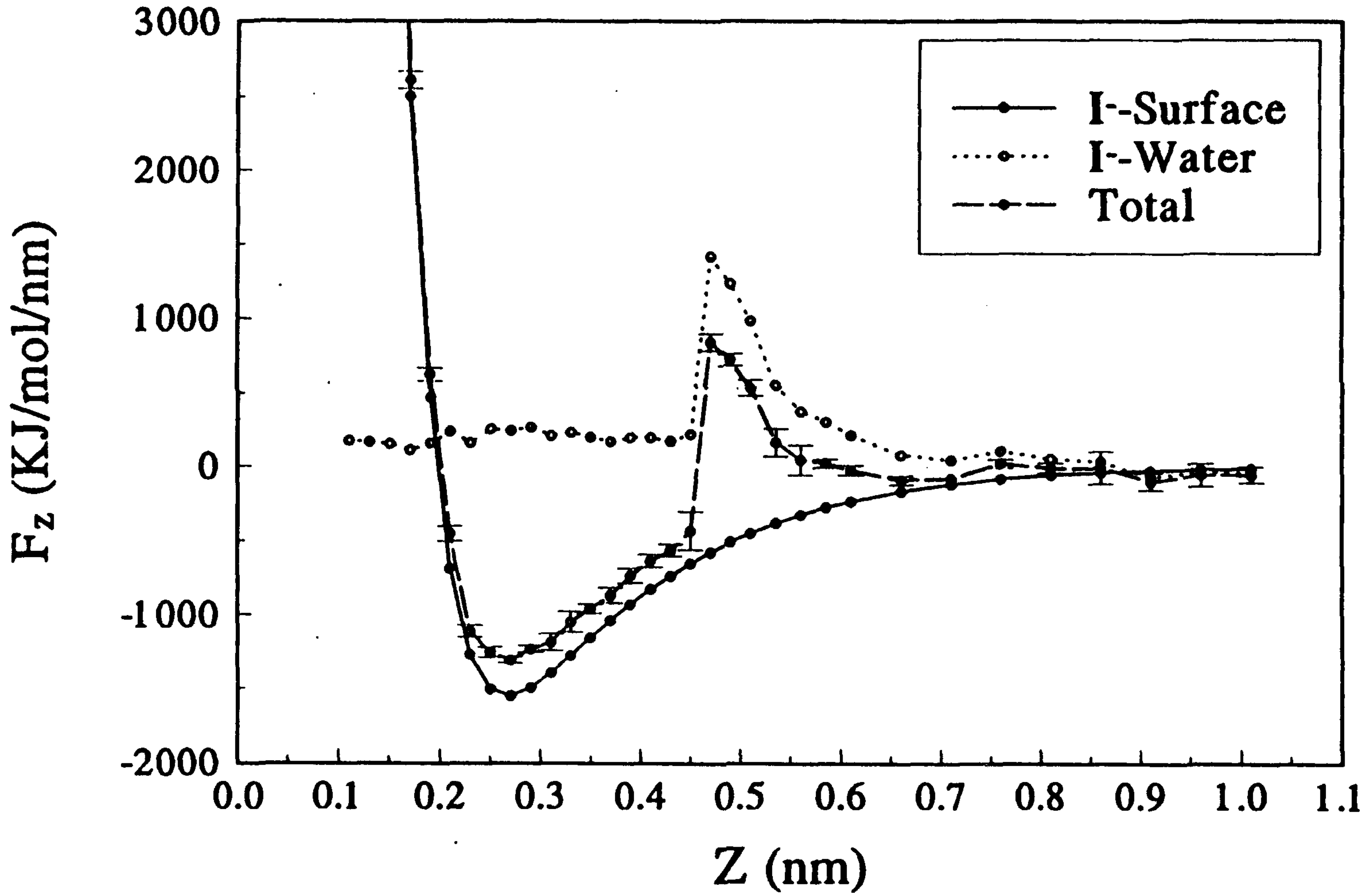
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Fig. 2.

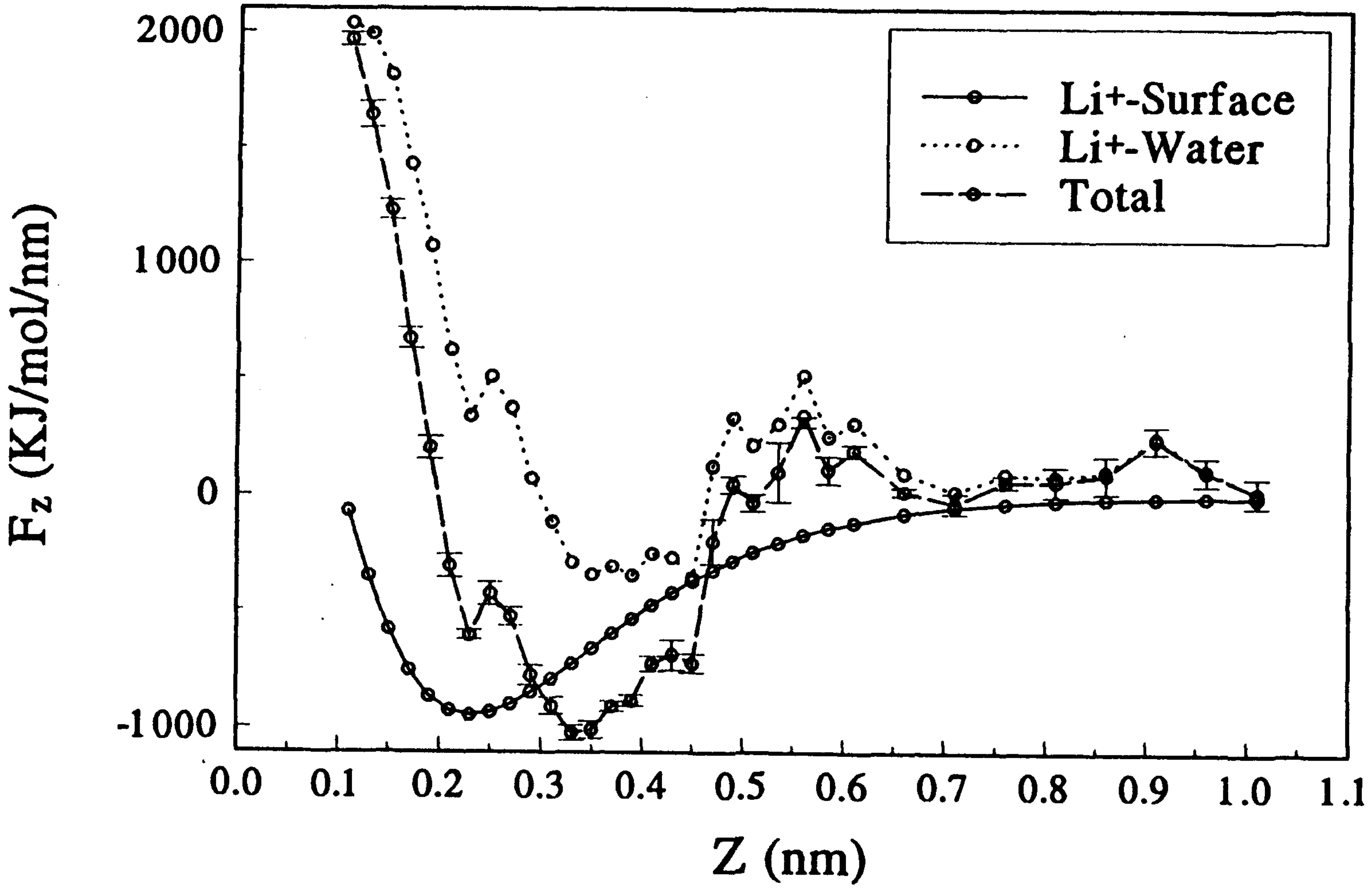
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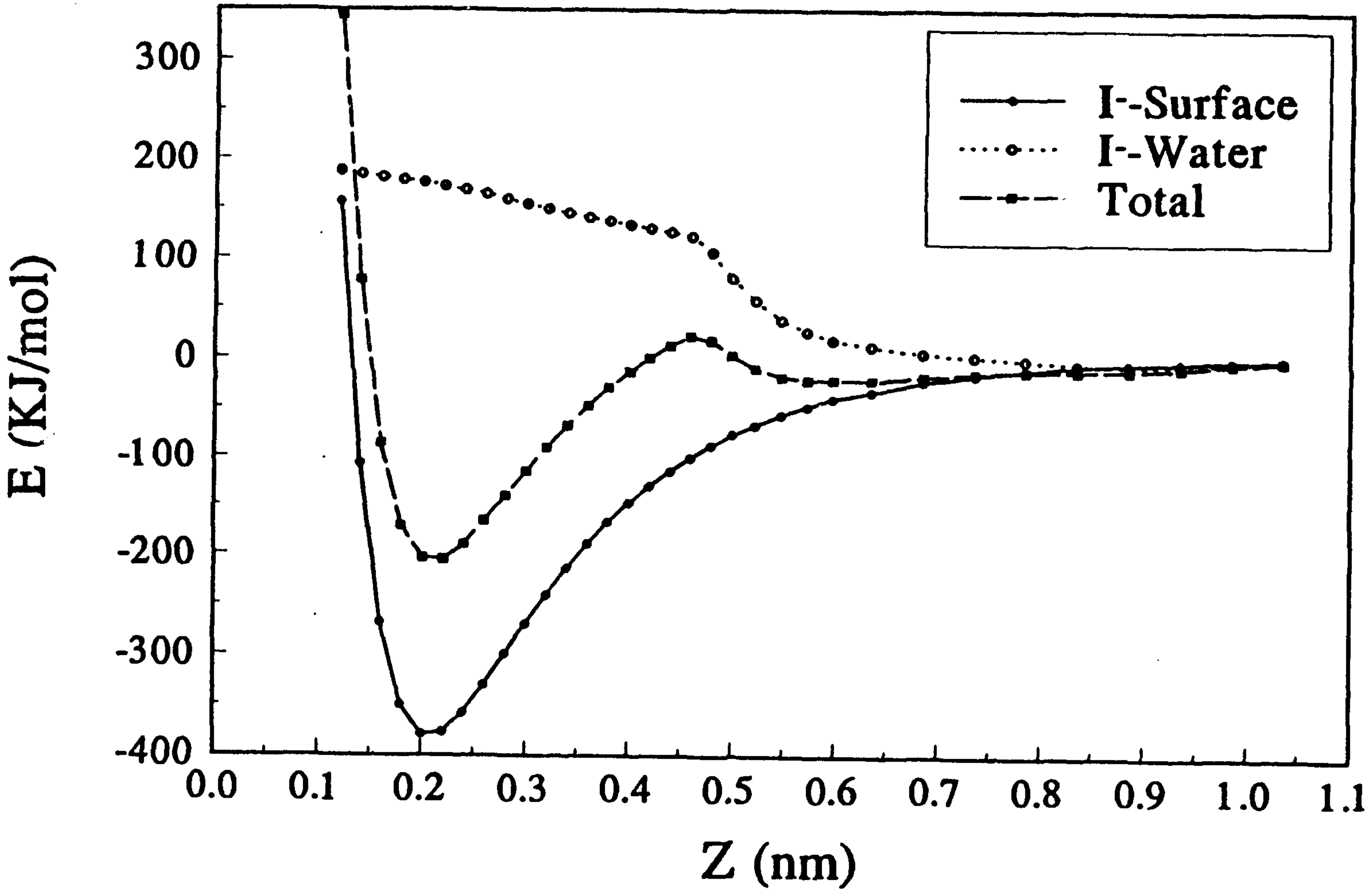
Fig. 3.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I^--Water
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Fig. 4.

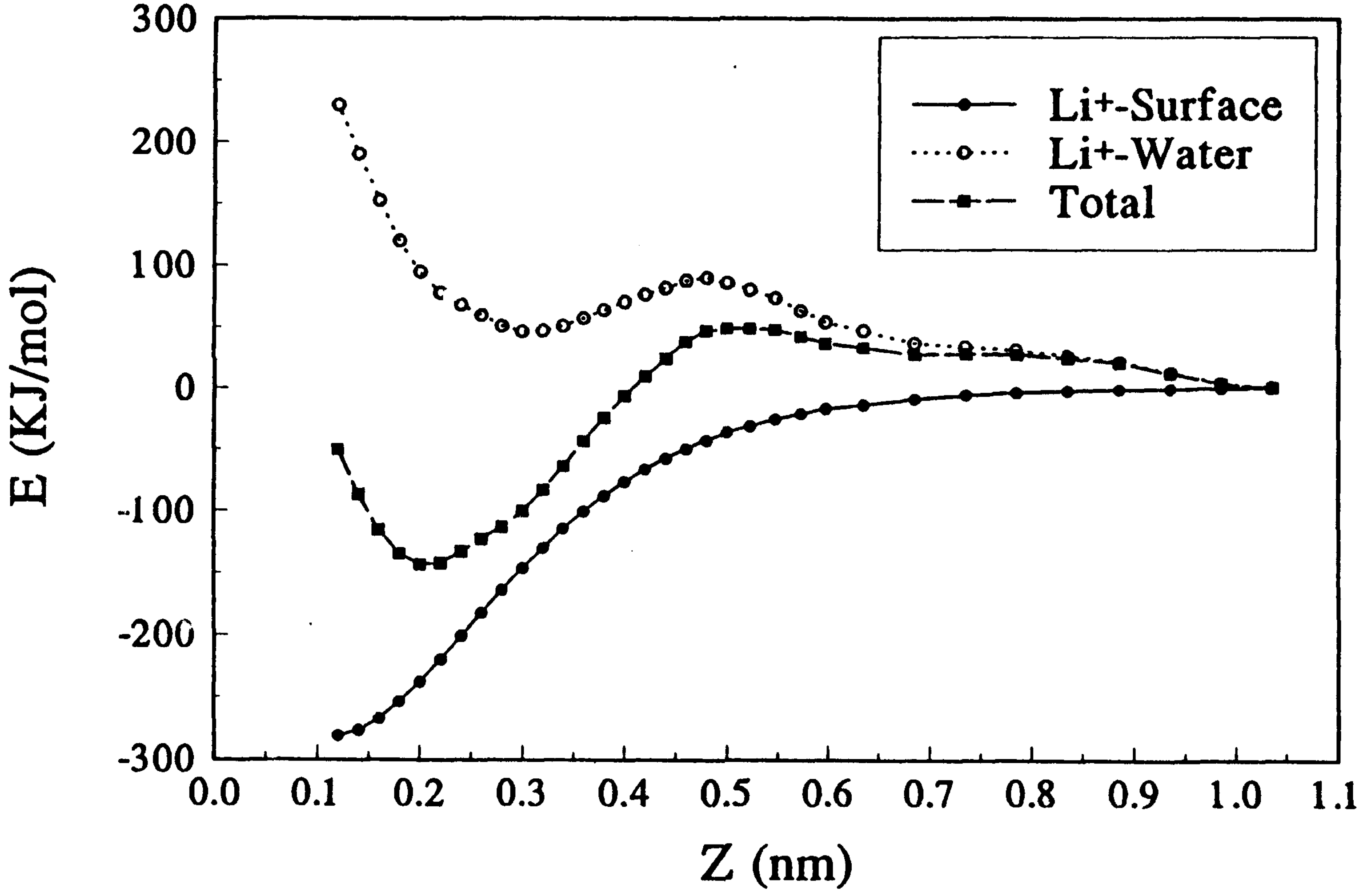
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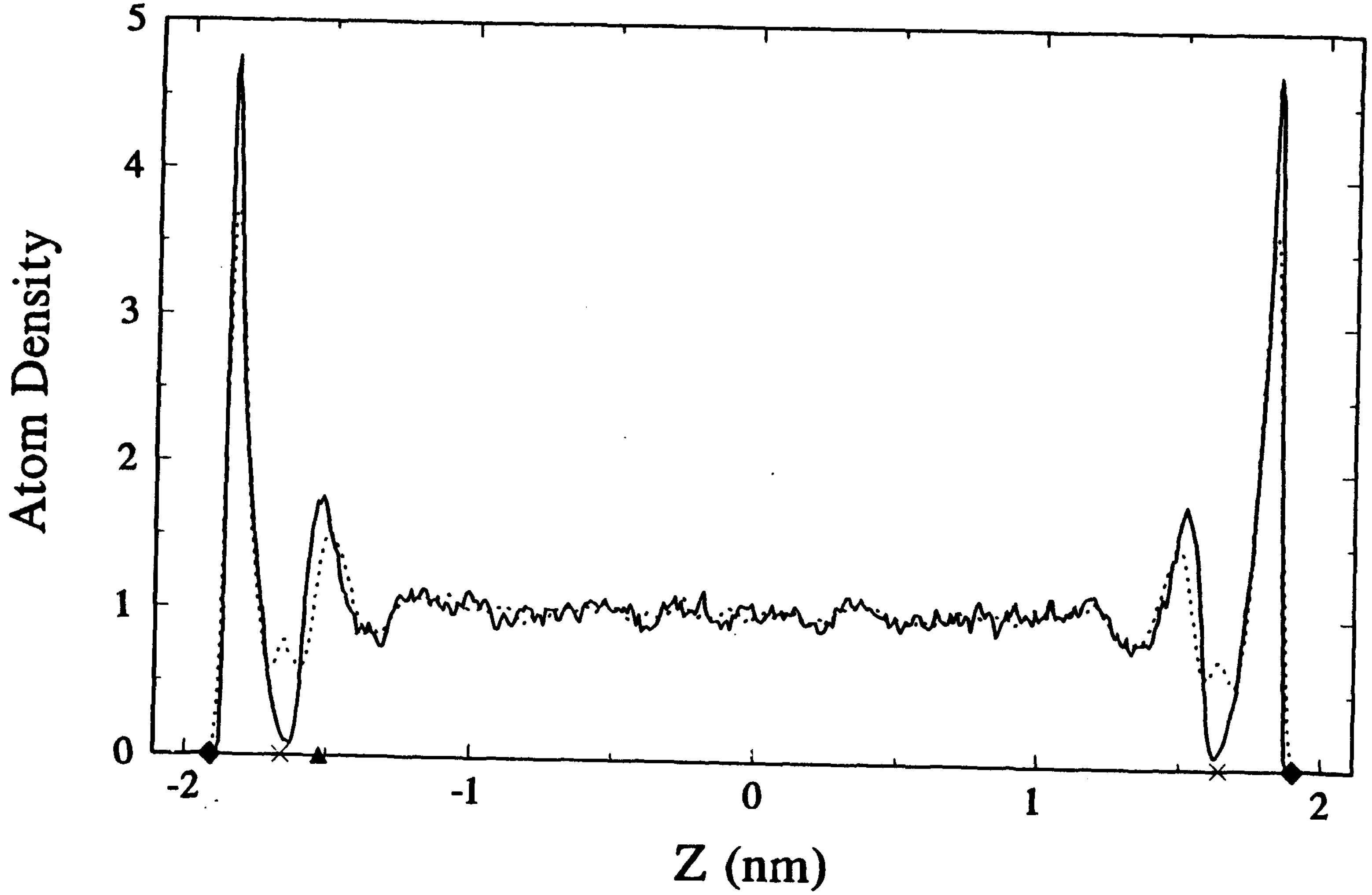
Fig. 5.



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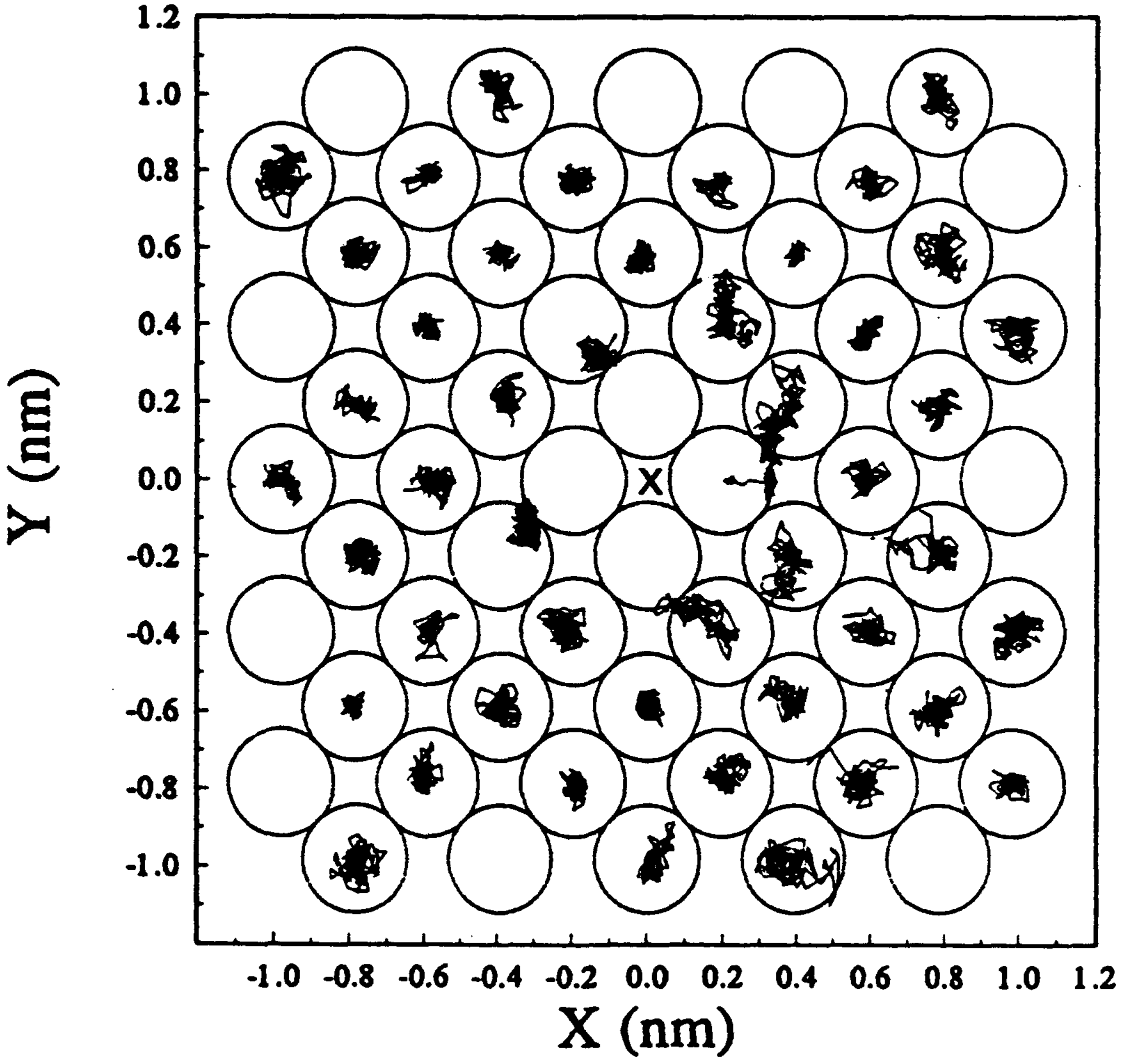

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Fig. 7.

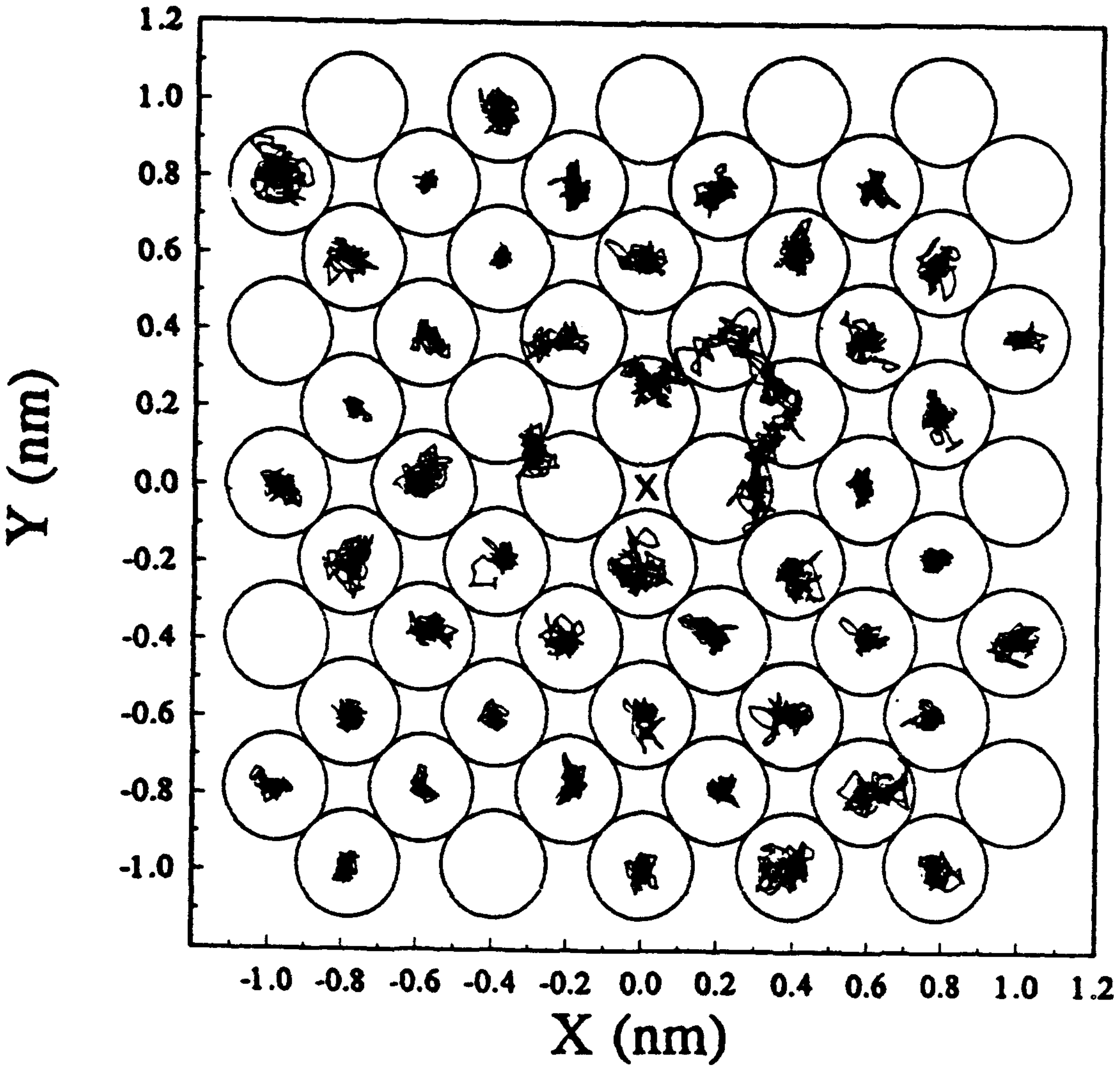
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Fig. 8.

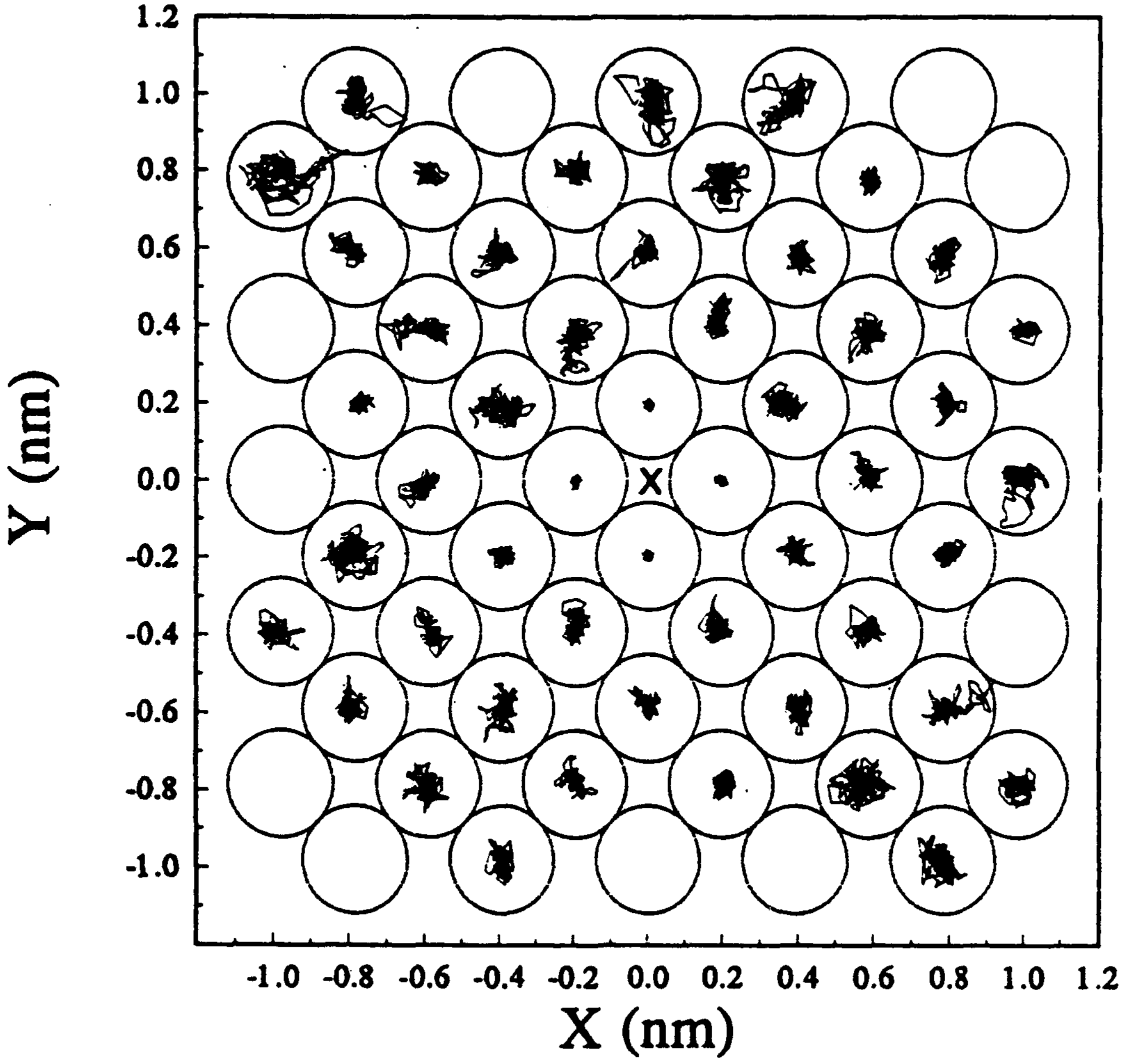
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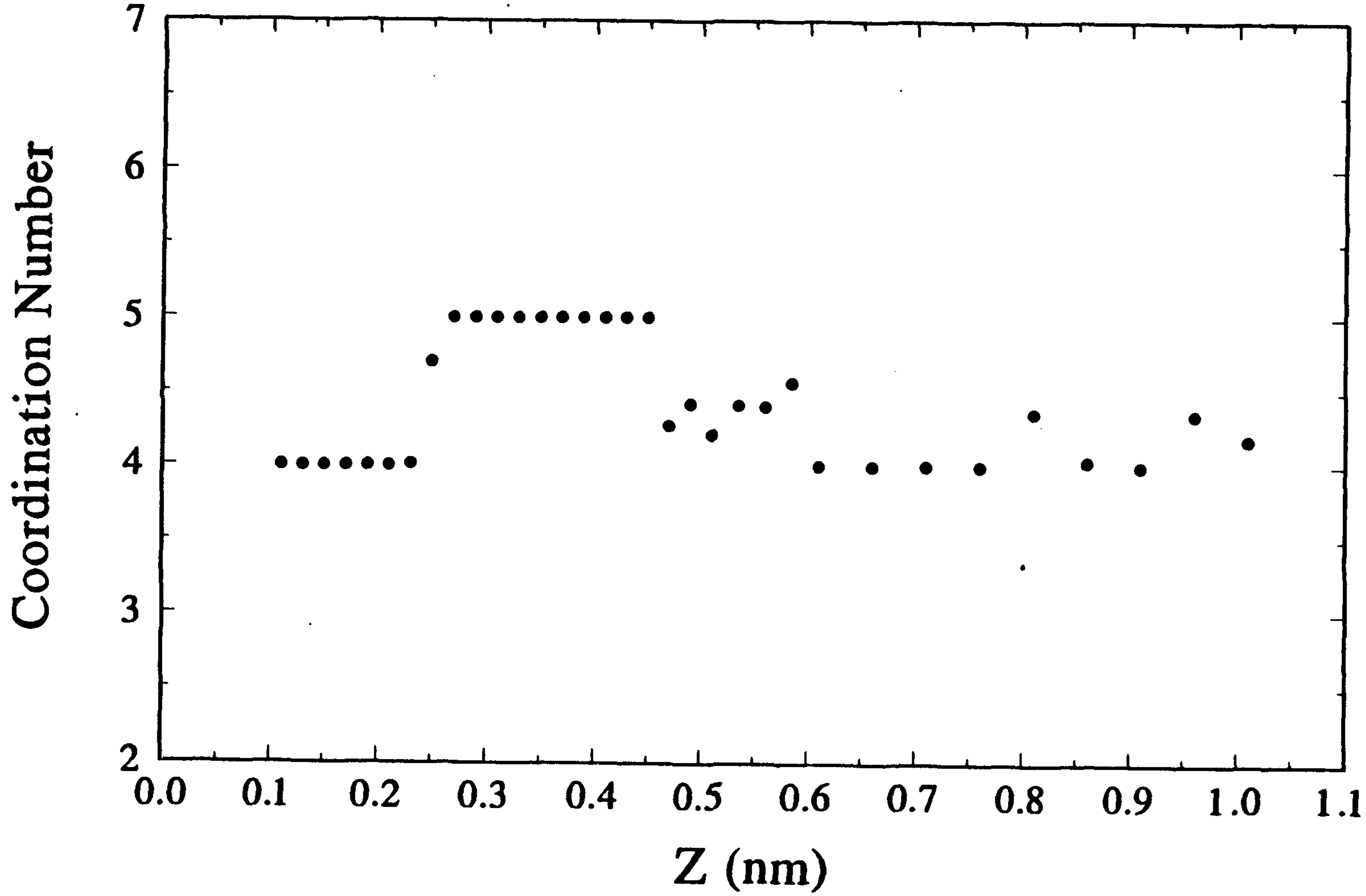
Fig. 9.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Z (nm)

Fig. 10.

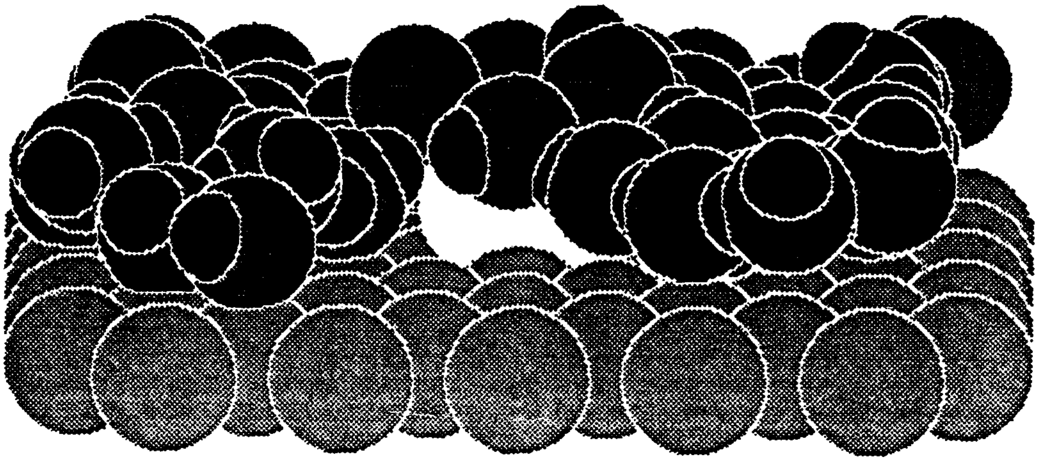

Fig. 11.