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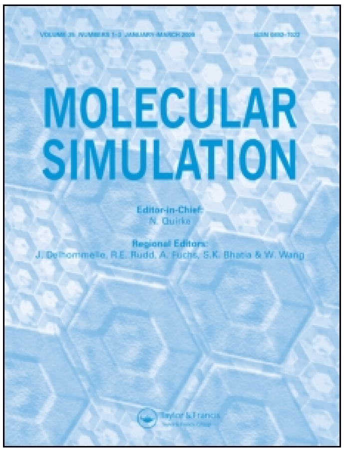

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MORPHOLOGY OF PLATINUM CLUSTERS BETWEEN GRAPHITE WALLS

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We report molecular dynamics simulations results for platinum atoms confined between two parallel graphite surfaces. The structural and thermodynamic properties of the platinum atoms are studied using gap widths in the range of 9 to $20\sigma_{pp}$. The results show that a small gap width will enhance the tendency of Pt atoms to form a single cluster or clusters with a well defined layered structure. For gap widths below $11.0\sigma_{pp}$ the number of Pt layers increases with the gap width and the energies of the system are affected accordingly. The Pt atoms are arranged in a FCC crystal structure with either the (110) or (111) faces exposed.

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I INTRODUCTION

Platinum is a versatile catalyst for many gas phase and liquid phase reactions of practical importance. Because of its high price, optimization in the effective use of platinum has been a major subject of research. Platinum is commonly supported inside a microporous inert material to enhance the contact surface area per weight of platinum. The size distribution and crystallinity of platinum will directly affect the effective use of the catalyst. In the catalysis of electrochemical reactions, carbon or graphite is often chosen as the support for platinum for its electrical conductivity and large surface area. Many experiments have reported the effect of morphology on the specific activity of platinum on carbon. Bregoli [1] has observed, for the catalytic reduction of oxygen, an increase of activity with the size of platinum particle supported. Sattler and Ross [2] reported maximum activity of platinum at about 3 to 5 nm. Watanabe *et al.* [3] observed, however, that the size of particle is important only when the intercrystallite distance is less than 20 nm. Kinoshita and co-workers [4] have reported that the change in activity is related to the change of relative fraction of platinum surface atoms on the (111) and (100) faces of the platinum particle. Bond [5] has reviewed the effect of particle size in a number of heterogeneous reactions. The morphology of platinum on carbon also changes with usage and some researchers have reported the loss of surface area of platinum over time. Bindra and Yeager [6] have observed the reorganization of platinum under electrochemical cycles. It is necessary to determine how the platinum distribution and morphology changes with platinum loading, size of the micropores, and other state variables. Furthermore, it is also important to find out how the platinum morphology will effect adsorption of reactant molecules and the specific activity of platinum in catalysis.

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Experiments with controlled and well defined micropores and uniform platinum loading are difficult. The microscopic characterization of platinum morphology is difficult although several attempts have been made to study platinum clusters on graphite using scanning tunnelling microscopy [7, 8, 9]. Theoretical modelling is a convenient tool to understand the details of the effect of molecular parameters and help to determine the optimum pore size and optimum platinum distribution. Many molecular simulation studies have been carried out to investigate the adsorption of gases on solid substrates [10, 11, 12, 13] as well as Lennard-Jones liquids confined in micropores [14, 15]. Few studies have been made for a platinum-substrate system. In an earlier study [16], platinum supported on microporous carbon was simulated by molecular dynamics calculations. For simplicity, a slit pore with two smooth carbon surfaces with platinum atoms in between were used as the model. The thermodynamics and phase transition of platinum inside a slit carbon pore of a fixed gap width were investigated using a Lennard Jones interaction potential. The effect of temperature has a marked effect on the structure of the platinum inside the slit pore. In this paper, we will investigate the effect of the width of slit pore on the structure and thermodynamics of the platinum cluster. This will hopefully cast some light to the effect of the size of the micropores on the effective use of the catalyst. At a fixed platinum loading, there is a pore size where transition from a filled pore to partially covered pore occurs. This will result in a large change of exposed platinum surface. The packing of adsorbed platinum will be analysed. These results will also serve as a basis of comparison in further catalysis studies where oxygen or other reactants are introduced.

II DETAILS OF THE SIMULATIONS

In this study, a simple model of the Pt-carbon wall system is used in the simulations. The details of the simulation and the intermolecular potentials are the same as in [16]. The two carbon walls are parallel to each other and are perpendicular to the z-axis. Normal periodic boundary conditions are maintained in the x- and y-directions. The dynamics of the system is controlled by Pt–Pt and Pt-wall interactions. The Pt–Pt interaction is represented by the LJ 12–6 potential:

$$\Phi_{pp}(r) = 4\varepsilon_{pp}\left\{\left(\frac{\sigma_{pp}}{r}\right)^{12} - \left(\frac{\sigma_{pp}}{r}\right)^{6}\right\} \tag{1}$$

where ε_{pp} and σ_{pp} are the well depth and the collision diameter for Pt–Pt interactions and r is the separation distance between the two Pt atoms. The Pt–Pt potential parameters used in this study have been adopted by other workers previously [17, 18, 19]. The values of ε_{pp}/k_B (k_B is the Boltzmann constant) and σ_{pp} being 7910 K and 2.54 Å respectively.

For the Pt-wall interaction, a simplified version of the 10–4 potential originally proposed by Steele [11] is used:

$$\Phi_{pc}(z) = 4\pi\rho_n\sigma_{pc}^6\varepsilon_{pc}\left\{\frac{\sigma_{pc}^6}{5z^{10}} - \frac{1}{2}\sum_{i=0}^{3}\frac{1}{(z+i\Delta z)^4}\right\} \tag{3}$$

where Δz is the distance between successive carbon layers which has a value of 3.35 Å [20] and ρ_n is the solid surface number density which has a value of 0.382 atoms/Å^2 [20]. The σ_{pc} and ε_{pc} are the potential parameters for Pt-wall interaction and the values are 470 K and 2.97 Å respectively. These parameters are obtained by using the Lorentz-Berthelot mixing rule. For this 10–4 potential, the Pt-wall interaction is calculated in a layer by layer manner. It has been shown to give comparable results [20] with the original Steele's potential which include the effects due to the spatial distribution of lattice atoms on the substrate surface.

We have carried out MD simulations using different gap widths (9–90σ_{pp}) between the two parallel carbon surfaces. All simulations were performed with a system containing 512 Pt atoms at reduced temperature ($T^* = Tk_B/\varepsilon_{pp}$) of 0.2. A low reduced density ($\rho^* = N\sigma^3/V$) of 0.0898 is chosen so that if all the platinum particles were adsorbed on both surfaces, a 40% to 90% monolayer coverage will occur. This also corresponds to experimental conditions of platinum loading on carbon surfaces. The initial configuration contains Pt atoms in an arbitrary regular lattice structure. Random velocities corresponding to a system temperature of $T^* = 1.0$ are assigned to each Pt atom. While no potential cutoff is imposed on the Pt-wall interaction, a potential cut off distance of 3.5 σ_{pp} was employed for the Pt-Pt interaction. The Verlet leap frog algorithm [21] was used to integrate the equations of motion.

The low temperature state is prepared by first equilibrating the system at $T^* = 1.0$ and then gradually decrease the temperature of the system to the specified temperature. The method employed is similar to that adopted by Berendsen *et al.* [22] in which the temperature of the system is lowered to the desired temperature gradually. In this work, we only allow the temperature to change by 0.001% during a MD step. As a result, a period of 500 ps of simulation time is typically required for the system to cool from $T^* = 1.0$ to 0.2. This roughly corresponds to a cooling rate of around 1×10^{13} °C/sec. After achieving the desired temperature, *ad hoc* temperature scaling is used to maintain the system at the desired temperature.

The structural characteristics of the Pt atoms are primarily examined through the density profile, $\rho^*(z)$, across the walls. The $\rho^*(z)$ is evaluated by dividing the space between the two walls into slabs of thickness Δz parallel to the walls. The number of Pt atoms in each slab, $n(z)$, is recorded during a simulation. The final number in each slab is then used to calculated the reduced density of that particular slab at the end of the run. The density profile, $\rho^*(z)$, between the two walls is given by

$$\rho^*(z) = \frac{n(z)\sigma_{pp}^3}{\Delta z L_x L_y N_{\text{sample}}} \tag{5}$$

where L_x and L_y are the x- and y-dimension of the system and N_{sample} is the number of samples taken during the run. The $\rho^*(z)$ presented in this paper is calculated from 200 slabs.

III RESULTS AND DISCUSSION

For the slit pores with a gap less than 11.0σ_{pp}, the structural characteristics of the Pt atoms are found to be consistent with our previous work [16]. The platinum atoms are

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organized into a single cluster with a layer structure as can be deduced from the evenly spaced and distinct peaks in the density profiles between the walls (Figure 1). The number of peaks or number of layers depend on the gap width of the slit pore. It increases stepwise from 8 peaks for a gap width of 9 σ_{pp} to 10 peaks for a gap width of 11.3 σ_{pp}. For a larger gap width of 20.0 σ_{pp}, two separate regions of adsorbed layers are formed. The density profiles are not as well defined and smaller secondary peaks can be found between two high peaks. In a few cases, the Pt atoms can also form a single large cluster next to a wall. Since the various runs are conducted at the same reduced density, the platinum loading per wall surface area is actually higher for a larger gap width. The breaking up into two clusters is due to competition of Pt–C and Pt–Pt interactions. From the perspective of maximum exposed platinum surface area, pores of 11.0 σ_{pp} or larger is therefore more desirable. This corresponds to 28 Å diameter in the pores of the carbon support. For a higher platinum loading or platinum density, the gap width for forming separate adsorbed clusters may be larger and this can be investigated in further studies.

The energetics of the platinum cluster in various widths of slit pores is also investigated. The results (Table 1) show that except for one or two discontinuities, the Pt-wall and the Pt–Pt potential energy become more negative as the width of the gap decreases (Figure 2). The trend of the decreasing Pt-wall potential energy is a result of the increase in the number of Pt atoms that are close to the graphite walls when the gap width is small. The trend of the Pt–Pt potential energy cannot be readily explained. This is because the mean Pt–Pt distance does not change significantly as shown in the $g(r)$ of different systems (Figure 3). However, the Pt–Pt potential energy might have a close correlation with the mean distance of adjacent Pt-layers.

The distance between the layer of Pt atoms adjacent to the graphite wall and the wall itself is found to be about 1.15 σ_{pp}. This distance corresponds to the minimum of the Pt-wall interaction potential ($r = 1.164\sigma_{pp}$). The separation distance of adjacent Pt layers is fairly even for systems with gap widths of less than 11.0 σ_{pp}. An estimation of this separation distance can be made based upon the number of Pt layers and the distance between the first layer of Pt atoms and the graphite wall.

$$\textit{Estimated separation Distance} = \frac{\textit{Gap Width} - 2 \times 1.164\sigma_{pp}}{\textit{No. of Pt Layers} - 1} \qquad (6)$$

where the distance of $1.164\sigma_{pp}$ is an approximate distance between the graphite wall and the first layer of Pt atoms. Figure 4 shows the variation of the mean distance between adjacent Pt layers with the gap width. The actual distances have the same trend as the estimated distances but the former is almost always smaller than the latter. For gap widths between 9 and 11 σ_{pp} the calculated Pt–Pt potential energy seems to have an opposite trend with respect to the interlayer distance. For LJ type of interaction potential, the optimal layer separation distance is 0.97 σ_{pp}. As a result, the Pt–Pt energy is more negative when the layer distance is close to this value. However, the change in potential energy is not large and the observed trend of the Pt–Pt potential energy may not be solely due to the inter-layer distance. The value of the total potential energy and the Pt–Pt energy may affect the dynamics and stability of the Pt morphology and the activity in electrocatalysis. The general

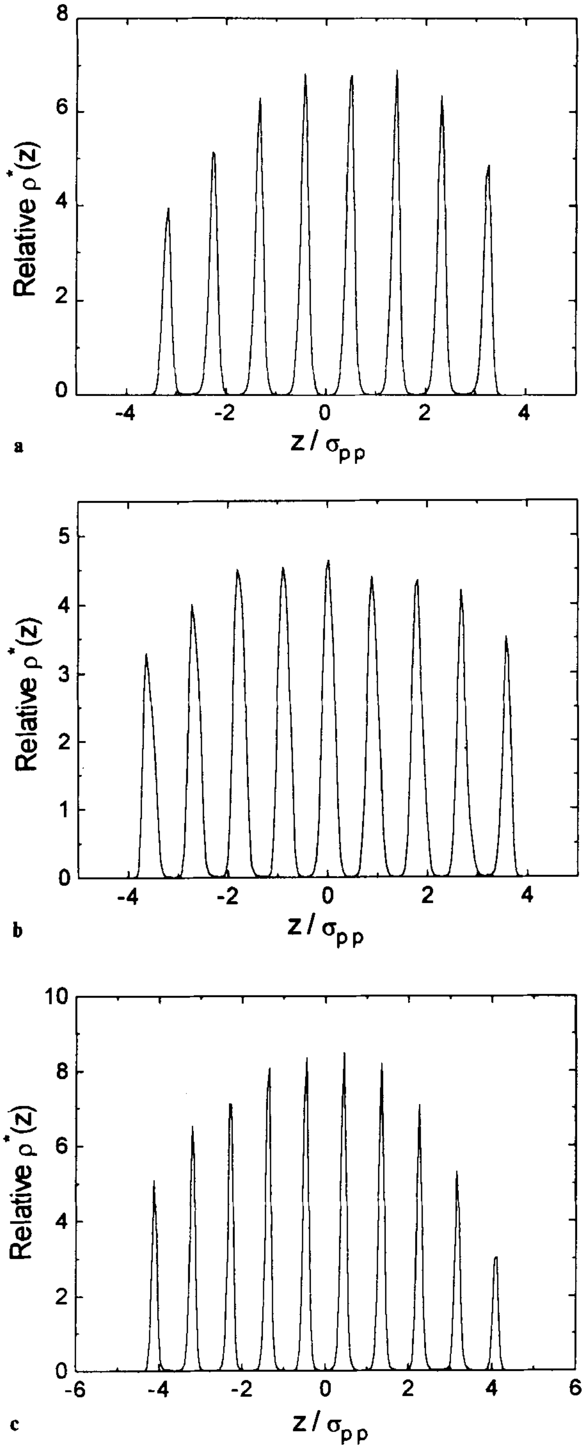

Figure 1 Relative density profiles between the walls for systems with gap widths of (a) 9.0, (b) 9.63, (c) 10.63 and (d) 20.0 σ_{pp}.

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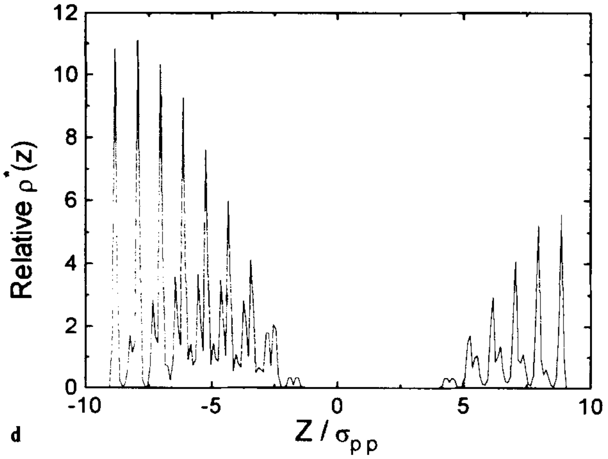

Figure 1 *(Continued.)*

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Table 1 The results of simulation using different gap widths

Gap Width/σ_{pp}	*Total*/ε_{pp}	*Pt-wall*/ε_{pp}	*Pt-Pt*/ε_{pp}	*KE*/ε_{pp}	*Layer Sep.*/σ_{pp}
9.0	−6.15	−0.180	−6.27	0.299	0.92
9.17	−6.14	−0.171	−6.27	0.299	0.85
9.63	−6.15	−0.163	−6.28	0.298	0.91
10.3	−6.09	−0.137	−6.25	0.299	0.90
10.63	−6.12	−0.131	−6.29	0.299	0.88
11.0	−6.07	−0.118	−6.26	0.300	0.90
12.0	−6.07	−0.172	−6.20	0.299	0.92
14.0	−6.06	−0.132	−6.23	0.299	0.79
16.0	−5.97	−0.129	−6.14	0.299	0.90
20.0	−5.89	−0.129	−6.06	0.299	0.90

observation here is the platinum is more strongly bound inside pores of smaller gap widths.

The crystal structure an crystal plane orientation of the Pt clusters is also examined by using the near neighbour angle analysis method [23,24]. In this method, the distribution of the angle θ between 3 adjacent atoms, i, j and k is calculated by the following formula.

$$\cos\theta = \frac{r_{ij}\cdot r_{ik}}{|r_{ij}||r_{ik}|}$$

where the separation distances $|r_{ij}|$ and $|r_{ik}|$ must be smaller than $1.3\,\sigma_{pp}$ which corresponds to a distance just beyond the first peak in the $g(r)$ of the Pt clusters. The near neighbour analysis is useful to distinguish the crystal structure of the cluster.

We have carried out the near neighbour angle analysis of the Pt clusters on three systems. The gap widths of the system are 9.17, 10.63 and $20.0\,\sigma_{pp}$ respectively. The distribution of interior angles θ for the $10.63\,\sigma_{pp}$ system is shown in Figure 5. The results

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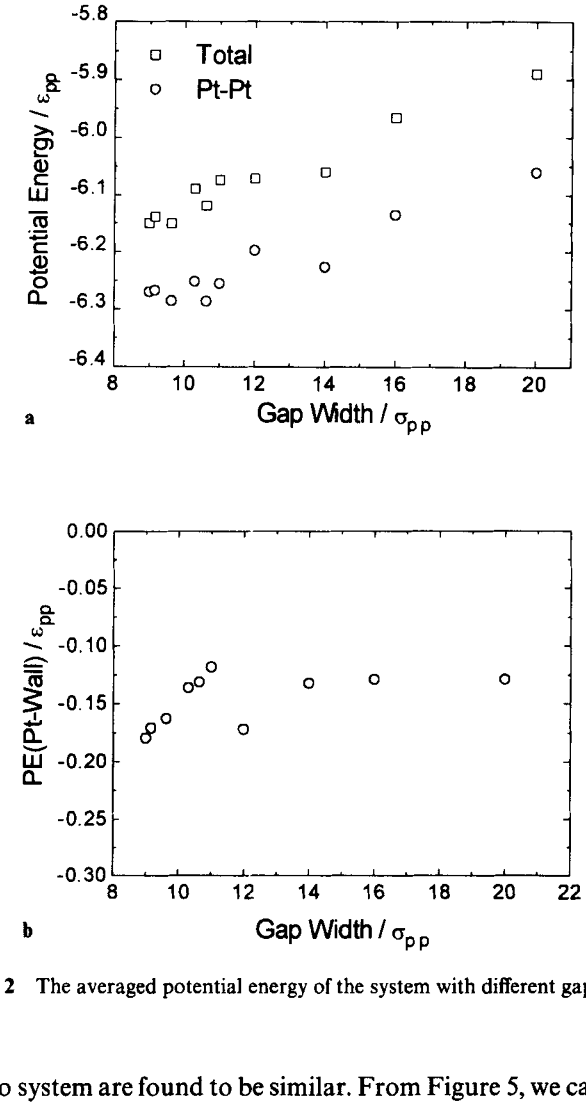

Figure 2 The averaged potential energy of the system with different gap widths.

for the other two system are found to be similar. From Figure 5, we can see that at high temperature ($T^* = 1.0$), the distribution is nearly flat except for a peak near 0.5 (which corresponds to an angle of 60 degrees). This peak is typical for LJ fluids as the LJ potential will favour equilateral triangles with $r_{ij} \approx r_{ik} \approx 2^{1/6}\sigma_{pp}$. At a lower temperature ($T^* = 0.2$), the distribution shows peaks at 0.5, 0.0 -0.5 -0.85, and -1.0. These peaks indicate FCC local ordering within the Pt cluster otherwise there should be an extra peak at $\cos\theta$ value of -0.33 for HCP local ordering.

The arrangement of the Pt atoms within the cluster can be studied by using the XY and XZ projections of the system. The arrangement of Pt atoms within the cluster was found to be similar for different gap widths. Here we examine a system with a gap width of 10.63 σ_{pp}. The XZ projection (Figure 6a) shows that the Pt atoms are concentrated in several regions parallel to the walls. This explains the distinct density peaks in the density profiles. The XY projection (Figure 6b) shows that the Pt atoms have

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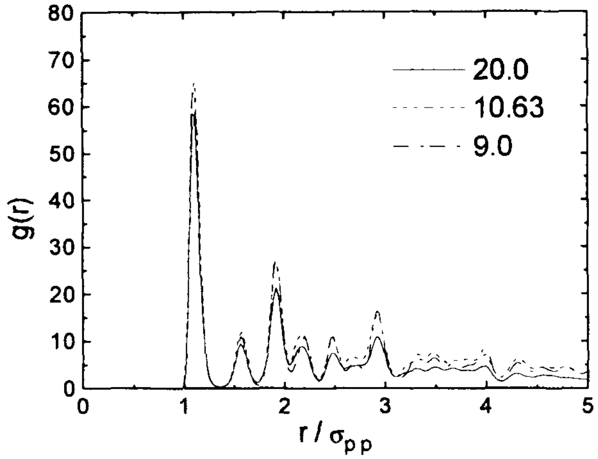

Figure 3 Pair distribution function, $g(r)$, of Pt particles in the system at gap widths of 20.0, 10.63 and 9.0 σ_{pp}.

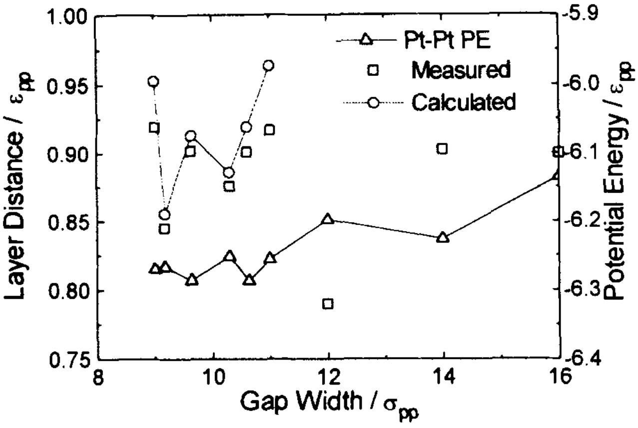

Figure 4 Comparison of measured and calculated distance between adjacent Pt layers.

a hexagonal arrangement within a layer. The packing of consecutive Pt layers seems to indicate that the cluster has an ABC structure. However, the crystal structure of the Pt clusters for systems with large gap width (> 11.0 σ_{pp}) is found to consist of rectangular arrangement within a layer and the stacking of the layers is of AB type. The structure of the Pt clusters in the system with a gap width of 9.0 σ_{pp} is also found to be this type (Figure 7). Since the crystal in found to be a FCC structure form the near neighbour angle analysis, the exposed surface would be (110) in the case of ABC packing and (111) in the case of ABA packing. No definite transition from ABC to ABA packing is concluded but it would be interesting to investigate the relative affinity for oxygen on these surfaces in future studies.

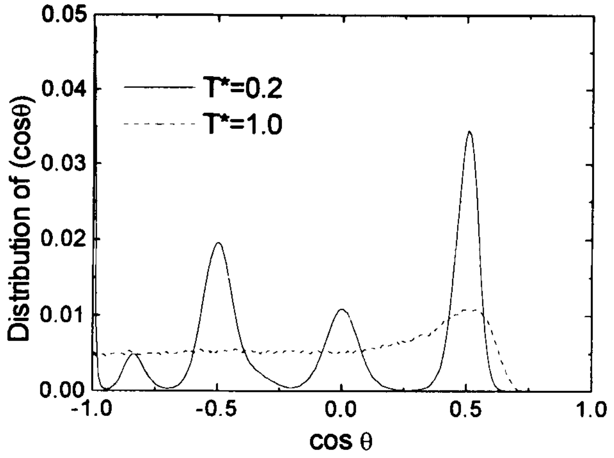

Figure 5 The distribution of $\cos\theta$ at temperature 1.0 and 0.2.

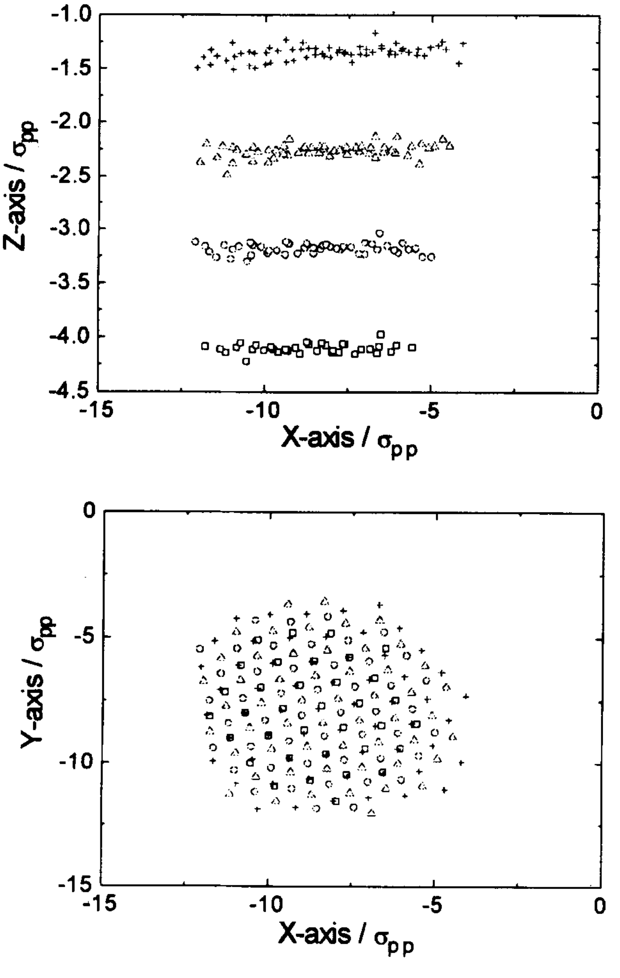

Figure 6 XY and XZ projection of the system with a gap width of 10.63 σ_{pp}.

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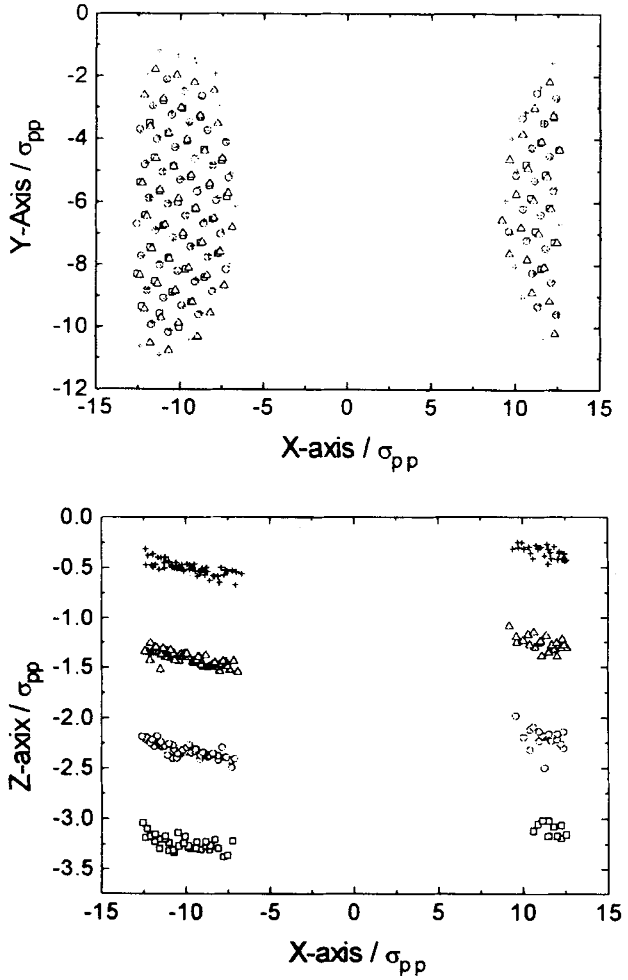

Figure 7 XY and XZ projection of the system with a gap width of 9.0 σ_{pp}.

No attempt has been made to study how the dynamics changes with density of Pt in the system and also the effect of a molecular graphite wall. We might expect a single cluster to be formed with a large gap ($> 11.0\,\sigma_{pp}$) when the Pt density is high or that a molecular wall will influence the packing of the Pt layers. These effects can be studied with further simulations.

IV CONCLUSIONS

In this study, we examined the structural and thermodynamic properties of the platinum atoms between parallel graphite walls gap widths in the range of 9 to 20 σ_{pp}. For the gap widths studied, the variation in the potential energy of the system is not large and no significant structural transition has taken place. The results show that the width of the gap has a significant influence on the structure of Pt clusters formed. Normally, Pt atoms will form a cluster with a layer by layer structure parallel to the graphite walls with distinct density peaks in the density profile. For pores larger than $11.0\sigma_{pp}$, separate adsorbed platinum clusters will be formed on each wall and will increase the exposed platinum surface area for catalytic action. In general, the platinum is more strongly bound inside smaller pores with a decrease in total potential energy and Pt–Pt energy. From the near neighbour analysis, the Pt atoms are arranged in a FCC crystal structure. The arrangement of atoms within a layer parallel to the wall can be hexagonal or rectangular and the stacking of different layers can be either AB or ABC. The corresponding exposed surfaces can be (110) or (111) faces of the FCC packing.

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