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An empirical interaction potential for the Ar/Pt(111) system

D. Kulginov and M. Persson*,

Department of Applied Physics,

Chalmers University of Technology and Göteborg University, S-412 96, Göteborg, Sweden

C.T. Rettner and D.S. Bethune,

IBM Research Division,

Almaden Research Center K31/801, San Jose, California 95120-6099, USA

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Abstract

We report an empirical potential energy surface (PES) for the Ar/Pt(111) system. We also report new atomic beam scattering data for this system, extending up to collision energies of > 7 eV. The PES is based on a pairwise sum of non-central potentials. Molecular dynamics calculations on this PES are found to be in generally good agreement with scattering data spanning the thermal and structure scattering regimes and with published measurements of the trapping probability as a function of incidence energy, $E_{\rm i}$, and angle, $\theta_{\rm i}$. An important exception to the overall good agreement between experiment and calculation is that we are not able to account fully for the observed degree of energy transfer for $E_{\rm i}\cos^2\theta_{\rm i} > 3$ eV. We suggest that the excess energy transfer is due to coupling to electron-hole pairs.

I. INTRODUCTION

When an atom or molecule collides with a surface, many outcomes are possible. [1] At low energy, the incident species may be trapped at the surface or scatter back into the gas phase. At high energy, new channels may open up, including sputtering and implantation. An understanding of such phenomena is needed as input in models for many important processes that occur at the gas-surface interface. In particular, such knowledge can aid the optimization of gas-surface chemistry and plasma etching, and in the design of thermonuclear reactors and spacecraft. In order to gain the necessary understanding of the gas-surface collisions in a given system, we need a detailed potential energy surface (PES), accurate over the relevant range of energies, and we need to appreciate dynamics of motion on that surface. Given the PES, the necessary dynamical information can be obtained by simulations, such as classical trajectory calculations or using wavepacket methods.

Estimation of an appropriate PES is far from routine, however, particularly for metal substrates, where the delocalized electrons make it difficult to describe accurately the true crystal surface. Calculating accurate gas-surface potentials for metal substrates from first principles remains a major challenge in surface science. Potentials can be calculated for atoms and molecules interacting with metal clusters and slabs using *ab initio* methods. Properties like the well depth are found to converge only slowly with cluster size, however. Slab calculations are somewhat better, but expensive. Müller [2] has calculated the PES for the Xe/Pt(111) system within the local density approximation (LDA) using a relatively large cluster of Pt atoms. Although the resulting potential places the minimum in the on-top site in agreement with other work, the resulting well depth is $\sim 20\%$ too large. More recently, Kirchner, Kleyn, and Baerends [3] have calculated the PES for the Ar/Ag(111) system for several different Ag clusters as well as for a three-layer Ag slab, all within the LDA. Although reasonably accurate, the well depth for the largest cluster, Ag_{19}, was still off by $\sim 20\%$ when compared to experiments. This type of discrepancy is expected for the LDA. [4] In the case of H_2 interacting with Al(110), [5] it has been found that the PES calculated within the

LDA can be improved significantly by inclusion of the generalized gradient approximation (GGA), which describes non-local exchange and correlations. Similar behavior has been seen for several other systems, including the interaction of H_2 with Cu surfaces, [6–8] and the interaction of CO with Pd(110). [9] In these latter cases, inclusion of the GGA correction to LDA gave potentials that were in significantly better agreement with experiments. The great expense of such calculations is a major drawback, however, limiting the number of configuration points that can be obtained. In addition, the GGA has been devised for chemical interactions and it is not clear that GGA will improve on the LDA description of physisorption interactions.

A valuable alternative to first principle calculations, in which experimental information is used only for guidance, is to construct the required PES empirically, relying heavily on experimental information. In this approach, a physically reasonable and flexible functional form of the PES is adjusted iteratively until calculated static and dynamical properties of the system match as wide a range of experimental data as possible. In most such studies, the emphasis has been on reproducing or rationalizing experimental results. A PES based on a sum of pair-wise central interactions may be sufficient for such purposes if the range of data is small. Experimental results that span a wide range of collision energies should provide information needed to construct a PES over a similarly wide energy range. Yet the task of finding a suitable form will be considerably more difficult. Barker and Rettner [10] have succeeded in using this method to obtain an accurate PES for the Xe/Pt(111) system. Calculations on the derived PES reproduced scattering, trapping, and desorption data, as well as detailed thermodynamic properties of the adsorbed monolayer. In this paper, we take a similar approach to obtain a PES for the closely related Ar/Pt(111) system.

The scattering experiments are described briefly in Section II while the measured data are compared with theory in Section IV B and discussed in Section IV C. The model for the empirical PES is introduced in Section III A and the details of the classical molecular dynamics is given in Section III B. The procedure to determine the potential parameters is presented in Section IV A. A comparison of calculated trapping probabilities with experimental data is made in Section IV D and some concluding remarks are given in Section V.

II. EXPERIMENTAL

The apparatus and techniques have been described in detail elsewhere, [11] but will be summarized here for completeness. Briefly, supersonic Ar beams are directed at a Pt(111) single crystal surface in a UHV chamber. The sample is held on a manipulator that permits accurate control of the surface temperature and incidence angle. The beam energy is varied by changing the nozzle temperature (up to 2200 K) and can be determined from atom flight times between a high-speed chopper and a differentially-pumped rotatable mass spectrometer [11]. The chopper is situated at a distance of 10.7 cm from the sample and rotates at 400 Hz to give beam pulses of about 7 μs FWHM. The rotating mass spectrometer is a further 10 cm from the sample. Time-of-arrival distributions at this detector are analyzed to obtain the energies of scattered species, as described elsewhere [11]. We also measure angular distributions of scattered atoms by rotating the mass spectrometer around the sample and recording the signal vs angle using phase sensitive detection referenced to the chopper.

III. MODEL

A. Interaction potentials

We model the atom-substrate PES by a branch representing the Pauli repulsion of the closed shell atom with the metal electrons and a branch representing the van der Waals attraction. Each branch is represented by a pairwise sum of non-central potentials and the PES is given by

$$V(\mathbf{r}, \{\mathbf{r}_i\}) = \sum_i v_{\mathrm{rep}}(|\mathbf{r} - \mathbf{r}_i - h_{\mathrm{r}}\hat{z}|) + \sum_i v_{\mathrm{vdW}}(|\mathbf{r} - \mathbf{r}_i - h_{\mathrm{a}}\hat{z}|) \tag{3.1}$$

where $\mathbf{r}$ is the position of the atom, h_{r} and h_{a} displace the force-center in the z-direction, $\hat{z}$, perpendicular to the surface and the summations are performed over all substrate atoms with positions $\mathbf{r}_i$. The repulsive pair potential has been choosen to have a simple Born–Mayer form given by

$$v_{\mathrm{rep}}(r) = A\mathrm{e}^{-\alpha r}, \tag{3.2}$$

while the attractive pair potential is given by

$$v_{\mathrm{vdW}}(r) = -D(r)\frac{C_6}{r^6}, \tag{3.3}$$

where the damping function,

$$D(r) = \begin{cases} \mathrm{e}^{-(r_0/r-1)^2}, & r \leq r_0, \\ 1, & \text{otherwise} \end{cases}, \tag{3.4}$$

represents the saturation of the van der Waals attraction when the atom comes closer than r_0 to a substrate atom.

The form of the PES in Eq. (3.1) is similiar to the functional form of the Xe–Pt(111) PES constructed by Barker and Rettner [12,10] but differs with respect to the repulsive branch. In their work this branch is modelled by a pairwise sum of central potentials describing the short range repulsion and a non-local flat potential that mimicks the interaction with the delocalized metal conduction electrons. We have not been succesful in using this flat potential since it involves many parameters and the available experimental data is insufficient to determine these parameters for the Ar/Pt(111) system. In particular, there is no experimental data available about the surface corrugation as contained in the measured "energy jump" at the transition from the incommensurate to the commensurate phase of Xe on Pt(111). Instead, we have just displaced the force center on the atom by h_{r} in the potential terms of the repulsive branch. This allows us to vary independently the corrugation, the steepness and the position of the repulsive wall in a simple manner with a minimal number of parameters. For the same steepness and position of the repulsive wall, it is possible to have a smaller potential corrugation than obtained from a pairwise sum of central potentials

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In the literature, there exist several different empirical potential models for the interaction of Ar with Pt(111) [14–18]. The study by Head-Gordon *et al.* [18] makes the most detailed comparison with available experimental data. Their model is based on a pairwise sum of Morse potentials and is able to reproduce measured low-energy scattering data, trapping-desorption data and the observed binding energy. The potential model developed by Smith *et al.* [17] and Lahaye *et al.* [16] represents the repulsive branch by a pairwise sum of Born-Mayer potentials and the attractive branch with a rigid van der Waals term which saturates close to the surface. The potential parameters in these two models were estimated from theoretical calculations on various levels of sophistication but no attempts were made to assess the potential models by detailed comparisons with available experimental data.

An interesting potential model has recently been constructed for Ar scattering from Ag(111) [19] using total energy calculations. This model is based on a pairwise sum of Born-Mayer potentials and a non-local z-dependent potential similiar to the one used by Barker and Rettner [12,13,10]. The potential parameters are adjusted in such a way that the resulting potential reproduces the potential energy surface of an Ar atom with a slab of Ag atoms as calculated within density functional theory using the local density approximation [3]. However, if the force field on the Ag surface atoms had been calculated within the same scheme there is no guarantee it would agree with that given by the proposed potential model.

We have used the same model as Arumanyagam *et al.* [20] for the forces between the Pt atoms. This force field is based on pairwise central potentials that are quadratic in the interatomic distances and include interactions up to second nearest neighbours [21]. This model reproduces the bulk Pt Debye temperature and the bulk phonon spectrum reasonably well. The force field has been truncated at the surface and no attempts have been made to account for the softening of the surface intralayer force constants suggested by inelastic He scattering [22] since this matter is a controversial issue [23].

B. Method of calculation

The calculations are based on molecular dynamics using a slab geometry with periodic boundary conditions. The Pt surface is represented by 4 layers with 24 atoms in each layer where the atoms in the fourth layer are clamped at their equilibrium positions. The range of both pairwise potentials in Eqs. (3.2) and (3.3) have been cut-off at a distance of 8 Å. The finite temperature of the slab is modelled in a similiar manner as Arumanyagam *et al.* [20] by Langevin dynamics. Random and friction forces, [24] as related by the fluctuation–dissipation theorem, [15] are applied in the vertical direction to the atoms in the third layer of the slab. The resulting stochastic equations of motion are solved by a variant of the Ermak algorithm that is consistent with the Verlet algorithm used to solve the deterministic equations of motion for the incident atom and the atoms in the remaining two layers of the slab. [25,26]

Some care is needed in the preparation of the initial state of the particle and the slab. The initial velocities of the Pt atoms have been randomly sampled from a Gaussian distribution with an average kinetic energy of $k_{\mathrm{B}}T$ in each coordinate while keeping the Pt atoms at their equilibrium positions. For these initial conditions the time needed for thermal equilibration of the slab has been determined from the temporal behaviour of the mean square displacements of the surface atoms and is found to be ~ 1.2 ps. This thermalization has been accounted for in the integration of the trajectories by starting the Ar atom at a distance from the surface where it takes more than the equilibration time until it collides with the surface. The lateral position of the Ar atom is randomly sampled over the slab surface. The integration of trajectories are finished either when the energy of the motion of the Ar atom normal to the surface is positive at a distance of 3 Å from the surface or when it is stuck with a total energy less than $-3k_{\mathrm{B}}T$. Sticking is found to be very rare at most temperatures and for incidence energies normal to the surface, E_{iz}, above 0.1 eV. However, multiple round trips in the potential well are accounted for in the calculation. The relative number of trajectories that have multiple turning points and are scattered within 5° from the scattering plane is more than ~ 1 % only for $E_{iz} \lesssim 0.25$ eV and $T \gtrsim 500$K.

The final angle and energy of the scattered atom is obtained from its final velocity after correcting for the refraction of the trajectory in the laterally averaged interaction potential. In our comparison with the measured scattering data reported in this work, the small angle of the detector aperture is accounted for in the calculation by collecting the results for Ar trajectories deflecting from the scattering plane (parallel to the $[1\overline{2}1]$ azimuth) by less than 5 degrees. The final scattering distributions are obtained by averaging over 5000 – 15000 trajectories within 2–3 degrees wide bins in the polar angle while 5 degrees wide bins are used to calculate the average final energies. In making the comparison with the scattering data measured by Hurst *et al.* [27], the only difference is direction of the scattering plane which is aligned along the $[10\overline{1}]$-direction.

The trapping probabilities have been calculated using 2000 trajectories and using the sticking criteria mentioned above. From this number of trajectories the estimated statistical uncertainities of the calculated probabilities are below 0.02. In these calculations, we have increased the lateral extension of the slab to comprise 8×12 atoms in each layer. This larger slab decreases the effect present at glancing angles of incidence that a trapped particle might pass the impact site several times in our slab geometry with periodic boundary conditions before the sticking criteria is fulfilled However, the energy deposited at the impact site is expected to have equilibrated before the particle passes this site again because a trapped Ar atom with a lateral energy of $\sim$50 meV takes about ~ 5 ps to cross the surface of the employed slab.

IV. RESULTS AND DISCUSSION

A. Potential parameters

The Born–Mayer parameters A and α in the repulsive branch of the potential have been determined from fitting the widths of the calculated angular distributions, $\Delta\theta_{\mathrm{f}}$, to the measured high incidence energy (1.5–7.3 eV) scattering data. In this energy regime, the influence of the attractive part of the potential on the scattering is expected to be negligible because the observed well-depth is less than 0.1 eV. Note that the remaining parameter h_r in this potential branch cannot be determined from the measured scattering data because the energy and momentum transfer is independent on h_r. This parameter and the remaining parameters of the potential have been determined from other available experimental and theoretical data on the Ar/Pt(111) system as detailed below.

At these high incidence energies, E_i, the $\Delta\theta_\mathrm{f}$s are dominated by the atom–surface potential corrugation. The parameters A and α tend to have compensating effects on this corrugation in the sense that for a given E_i and θ_i it is possible to keep the same value of $\Delta\theta_\mathrm{f}$ when increasing α by increasing A. These effects have been partially disentangled by considering the dependence of $\Delta\theta_\mathrm{f}$ on both E_i and θ_i. For $E_i > 1.5$ eV and at 800K, the angular distributions for all θ_i are satisfactorily reproduced for α in the range 2.8-3.3Å^{-1} with appropriate values for A. Larger values of α than 3.3Å^{-1} make $\Delta\theta_\mathrm{f}$ increase too slowly with increasing E_i and decrease too slowly with increasing θ_i. At T=85K and for $E_i = 1.63$ eV, on the other hand, the calculated $\Delta\theta_\mathrm{f}$ is too broad compared to the measured $\Delta\theta_\mathrm{f}$ for the range of α suggested by the high temperature data and can only be reproduced by a larger value of α. Thus we have made a compromise by choosing a value of 3.3Å^{-1} for α.

The deduced values for A and α, as listed in Table I, are in close agreement with the corresponding parameters of the repulsive part of the Morse potential in the model developed by Head–Gordon *et. al.* [18] The value of α is also close to the corresponding values in the Born–Mayer potentials proposed by Smith *et. al.* [17] and Lahaye *et. al.* [16] while the repulsive parameter A has in both cases a quite different value.

The position of the repulsive wall for the interaction of the Ar atom with Pt surface atoms can be varied independenly of A and α by h_r and, as stressed above, h_r cannot be determined from the scattering data alone. The value of $h_\mathrm{r} = 0$ corresponds to a repulsive branch represented by pairwise central potentials and yields an unreasonably large value of about 3.7 Å (at a potential energy of 0.1 eV corresponding to the well-depth) for the interaction radius of the Ar–Pt dimer compared with the radius about 3.0 Å deduced from the sum of van der Waals radii. This fact was also noted by Head–Gordon *et. al.* [18] in their potential model and suggests a value of ~ -0.7 Å for $h_{\rm r}$. This negative value for $h_{\rm r}$ results in a smaller potential corrugation for the Ar–Pt surface interaction than expected from a pairwise sum of central potentials with the same laterally averaged repulsive potential. This effect is demonstrated in the LDA calculations by Kirchner, Kleyn and Baerends [3] of the interaction energy of Ar with different Ag atom clusters and a slab of Ag atoms and is caused by the lateral smoothing of the interaction of the closed shell Ar atom with Ag surface ion–cores by the valence electrons (see also Ref. [28] for an analogous effect for the K^+–W(110) interaction). For instance, the repulsion is found to be larger at an hollow site than expected from a pairwise sum of the calculated Ar–Pt dimer potentials. This picture is confirmed by results from recent LDA calculations by Kirchner [29] for the interaction energies of the Ar–Pt dimer and a Ar–Pt tetrahedral cluster. In fact, this calculation gives a position of the repulsive wall that corresponds to $h_{\rm r} = -0.75$ Å and with a steepness that is in good agreement with our model for the repulsion.

The value of the van der Waals parameter C_6 is choosen such that the laterally averaged potential reproduces the corresponding van der Waals potential evaluated by Smith *et al.* [17] from the polarizability of the Ar atom and the dielectric function of platinum. The remaining parameters $h_{\rm a}$ and r_0 in the attractive potential branch are choosen to reproduce the measured values for the well-depth of about 80 meV [18] and the vibrational frequency of the adsorbed atom of about 5 meV by Comsa *et al.* [30] The resulting values for all these van der Waals parameters are listed in Table I.

The proposed potential energy function predicts the equilibrium position to be at the hollow site with a small potential barrier ~ 5 meV at the top and bridge sites. However, we do not think that this empirical potential energy function is able to predict this detail of the PES. More experimental information is needed about the surface corrugation at low energies. In the case of the Xe-Pt(111) system, this information, as contained in the measured "energy jump" at the transition from the incommensurate to the commensurate phase, was crucial to determine unambigously the adsorption site.

B. Comparison with scattering experiments

The quality of our potential model is here demonstrated by a detailed comparison between calculated and measured angular and mean final energy distributions shown in Figs 1–8. This comparison will mainly concern the experimental scattering data reported in this work but we will also make a direct comparison in Fig. 9 with some of the low-energy scattering data measured and parametrized by Hurst *et al.* [27].

The good agreement between the measured high temperature $\Delta\theta_{\mathrm{f}}$ for $E_{\mathrm{i}} \gtrsim 1.5$ eV at the three different angles of incidence, 30, 45, and 60°, with calculated $\Delta\theta_{\mathrm{f}}$, shown in Figs 1–3, is quite remarkable in view of the large range of E_{i} and θ_{i} and with only two Born–Mayer parameters in the repulsive potential. The behaviour of the positions of the maxima of the angular distributions and their shapes with E_{i} and θ_{i}, is a prediction of the model and is, in this energy regime, in good agreement with experiments. Minor discrepancies between calculated and measured distributions show only up in the energy region $E_{\mathrm{i}} \lesssim 1.7$ eV.

The effects of the temperature on the angular distributions, as can be seen both in Fig. 4 and from a comparison between the results in Figs 1 and 5, show that the calculations have varying degree of success to reproduce the variation of $\Delta\theta_{\mathrm{f}}$ with surface temperature T. The observed $\Delta\theta_{\mathrm{f}}$ tend to increase more rapidly with T than the calculated $\Delta\theta_{\mathrm{f}}$. In particular, these discrepancies are biggest for the highest energies in Fig. 5 at T=85K. However, at this low temperature well below the Debye temperature the effect of quantum statistics of the phonon modes on the scattering might be important and needs to be estimated.

In Figs 6–8, we make a direct comparison between calculated and measured average final energy, $\langle E_{\mathrm{f}}\rangle$, as a function of final scattering angle θ_{f}. The agreement between theory and experiments is good except at high energies for the perpendicular motion of the Ar atom, $E_{\mathrm{i}}\cos^2\theta_{\mathrm{i}} \gtrsim 3$ eV, where the theory gives too low energy transfer, in particular for θ_{f} around the specular direction, $\theta_\mathrm{f} = \theta_\mathrm{i}$. This discrepancy is quite unexpected in view of the finding that the shapes of the measured angular distributions are so well reproduced at these high energies. In Section IV C, we will discuss a possible physical cause behind this discrepancy.

In Fig. 9, we show some representative examples of comparisons of the calculated angular and average final energy with the parametrized data measured by Hurst *et al.* [27]. As illustrated in Fig. 9 for a few representative scattering conditions, we find that the agreement to be rather good to excellent for $E_\mathrm{i} \gtrsim 0.13$ eV up to their highest $E_\mathrm{i} \sim 0.34$ eV where the temperatures are all in the range ~ 500 to $\sim 900K$.

We close this section by making a few remarks on how well the measured scattering data for the Xe/Pt(111) and Ar/Ag(111) system are reproduced from results using potential models. The most extensive comparison has been made by Barker and Rettner [12,10] for scattering of Xe from Pt(111) and includes a wide range of E_i from ∼0.5 to ∼14 eV, several different angles of incidence and a range of temperatures from 200 to 800K. The calculations based on their potential model are able to reproduce very well the detailed shapes of the measured angular distributions and also the different forms of $\langle E_\mathrm{f} \rangle$ with θ_f. There are only some minor discrepancies at the lowest E_i with respect to the position in the maxima of the angular distributions and at the very highest E_i the measured $\langle E_\mathrm{f} \rangle$ is about 15% smaller than the calculated $\langle E_\mathrm{f} \rangle$. For the Ar/Ag(111) system the comparison made by Lahaye *et. al.* [19] is limited to an incidence energy range of 0.2 to 2.6 eV for a single angle of incidence, while the potential model is derived from LDA. The calculated $\Delta\theta_\mathrm{f}$ reproduce the measured trend with E_i but are about 5–10° larger than the measured $\Delta\theta_\mathrm{f}$. The calculated shapes of $\langle E_\mathrm{f} \rangle$ as a function of θ_f are in good agreement with experiments but the magnitudes of the calculated $\langle E_\mathrm{f} \rangle$ are about 20–30% too large.

C. Scattering dynamics

In order to understand the behaviour of the measured scattering data and to discuss some of the causes behind the discrepancies between theory and experiments it is necessary to discuss the dynamics behind the energy and momentum transfer for the scattering of Ar from Pt(111). A more or less complete picture of the scattering dynamics of similiar systems, involving closed shell interactions, like Xe from Pt(111) [12,13,10] and, more recently, Ar from Ag(111) [19] has been obtained from studies based on molecular beam experiments and molecular dynamics calculations. The scattering was found to be characterized by two different regimes referred commonly to as the thermal and the structure scattering regime. We will show that these two regimes are clearly discernable in our data for Ar/Pt(111) and they will now be discussed in turn.

A characteristic feature of the thermal scattering regime for scattering from flat surfaces such as Pt(111) is the approximate conservation of lateral momentum in the scattering. This regime is attained at low E_{i} where the classical turning point for the incident atom is far away from the surface and the atom experiences a low potential corrugation. Lateral momentum conservation imposes a direct relation between the final energy, E_{f}, and scattering angle, θ_{f}, which is given by,

$$\frac{E_{\mathrm{f}}}{E_{\mathrm{i}}} = \left(\frac{\sin\theta_{\mathrm{i}}}{\sin\theta_{\mathrm{f}}}\right)^2 . \tag{4.1}$$

This relationship is indicated in the Figs. 6–9 which shows that lateral momentum conservation is nearly obeyed for the measured data at $E_{\mathrm{i}} = 0.2$ eV and $\theta_{\mathrm{i}} = 45°$ in Fig. 7 and for all the low-energy data in Fig. 9. Another characteristic feature of the thermal scattering regime is the rapid increase of $\Delta\theta_{\mathrm{f}}$ with decreasing E_{i} which is evident in Figs. 1 and 5. These figures show also that there is a strong increase of $\Delta\theta_{\mathrm{f}}$ with temperature and that the maxima of the angular distributions also shifts from super- to subspecular θ_{f}. All these salient features are related to the approximate lateral momentum conservation and can be rationalized in a simple hard cube model. [31,32] The shape of the angular distribution is determined by normal momentum transfers associated with thermal spread of cube velocities. Thus $\Delta\theta_{\mathrm{f}}$ increases with temperature and this effect becomes less important as E_{i} increases. Sub-specular scattering follows collisions in which the cube is moving “outwards”, which results in energy gain and the skewed shape of the angular distribution reflects the non-linear kinematical dependence between θ_f and normal momentum transfer.

This discussion of the thermal scattering regime shows that it is necessary to have a good model of the surface lattice dynamics to reproduce the measured $\Delta\theta_\mathrm{f}$. As already discussed in section III A, the present model might not be sufficiently accurate for this purposes. Moreover, the fact that the $\Delta\theta_\mathrm{f}$ are dominated by the contribution from the surface vibrations makes it difficult to determine the potential corrugation at low E_i by a comparison with calculated $\Delta\theta_\mathrm{f}$.

At higher energies, the atom experiences a larger potential corrugation since the turning-point for the incident atom comes closer to the surface ion-cores which causes the lateral momentum conservation to break down. This effect is clearly seen in Figs 1-3 for $E_\mathrm{i} \gtrsim 1.5$eV where $\langle E_\mathrm{f}\rangle$ is much less for superspecular θ_f than expected from the result in Eq.(4.1). In fact, the behaviour of E_f resembles more the result, indicated in these figures for a binary collision between two hard spheres, as given by,

$$\frac{E_\mathrm{f}}{E_\mathrm{i}} = \left(\frac{\cos\theta - \sqrt{\alpha^2 - \sin^2\theta}}{1+\alpha}\right)^2, \tag{4.2}$$

where $\theta = \theta_\mathrm{i} + \theta_\mathrm{f}$ is the total scattering angle and $\alpha = \frac{m_\mathrm{Pt}}{m_\mathrm{Ar}}$ is the mass-ratio between a Pt and an Ar atom.

A characteristic feature of the structure scattering regime, dictated by the increase of the potential corrugation with E_i, is the increase of $\Delta\theta_\mathrm{f}$ with E_i, as can be seen in Fig. 1 for E_i in the range 5–7 eV. For the larger θ_i in Figs 2 and 3, the energies for the perpendicular motion are not sufficiently large, for the contribution from the potential corrugation to $\Delta\theta_\mathrm{f}$, to dominate over the contribution from surface vibrations. In this transition regime between the structure scattering and thermal scattering the net result of these two counteracting contributions with respect to E_i is to produce $\Delta\theta_\mathrm{f}$ that are almost constant over a relative large range of E_i. The result that the calculated angular distributions for E_i=0.67 and 1.63 eV at $\theta_\mathrm{i} = 30°$ in Fig. 5 are appreciably broader than the measured distribution is probably an effect of too large potential corrugation in the model at these energies.

In the structure scattering regime, the main features of the average final energy and the angular distribution of the scattered atoms can be understood from calculating in-plane trajectories at zero temperature. At this temperature, the in-plane distributions arise only from trajectories that impact along the azimuth $[1\overline{2}1]$ which passes through top, hollow and bridge sites. The results for E_{f} versus θ_{f}, obtained for these in-plane trajectories, form closed $E_{\mathrm{f}}(\theta_{\mathrm{f}})$-curves whose shapes give useful insight into the scattering dynamics [33]. Examples of such curves for different surface corrugations are shown in Figs. 10 and 11. The lower branch of the $E_{\mathrm{f}}(\theta_{\mathrm{f}})$-curve in Fig. 10a) arises predominantly from the scattering from a single surface atom and is close to the binary collision result in Eq.(4.2). The lower energy transfer on the upper branch of this curve is due to the simultaneous interaction with three neighboring surface atoms near the hollow sites while the somewhat larger energy transfer in the loop on this branch is due to the simultaneous interaction with two surface atoms close to the bridge site. At lower potential corrugation, the $E_{\mathrm{f}}(\theta_{\mathrm{f}})$-curve narrows in angle and shifts upwards in energy and the loop in the upper branch decreases as shown in Fig. 10b). At larger corrugation the angular spread increases and the shape of the $E_{\mathrm{f}}(\theta_{\mathrm{f}})$-curve changes qualitatively, as shown in Fig. 11, when the turning point of the atom comes so close to the surface ion-cores that the interactions with these ion-cores become separated in time corresponding to multiple collisions. These collisions make the final angular spread very broad and result in more efficient energy transfer than can be obtained in a binary collision.

The behaviour of the E_{f}-curve with impact parameter determines the final in-plane angular and average final energy distributions which are shown in Fig. 10a). The rainbow singularities at the four turning points of the $E_{\mathrm{f}}(\theta_{\mathrm{f}})$-curve have also been identified in the calculations of the Ar–Ag(111) scattering intensity from a static (zero temperature) surface by Lahaye *et al.* [19] At high temperatures like 800 K, the surface vibrations smear out these rainbow singularities and the shape of the angular distribution becomes structureless but with a $\Delta\theta_{\mathrm{f}}$ that is approximately the same as at zero temperature. The effects of temperature on the average final energy, on the other hand, is very small and amounts only to the developments of wings at the far ends of the corresponding zero temperature curve.

In the structure scattering regime, the main discrepancy between the calculated and measured scattering data is that the calculated average energy transfer is lower than that measured. We have not been able within our potential model to account for the measured $\langle E_{\mathrm{f}} \rangle$ in the range $E_{\mathrm{i}} \cos^2 \theta_{\mathrm{i}} \gtrsim 3$ eV without making the potential corrugation so strong that multiple collisions are introduced which give rise to a broad and irregular angular distribution that is inconsistent with the measured data. We do not think that this is a problem of our specific potential model; it is difficult to understand how energy transfers close to the values obtained in binary collision can give rise such narrow angular distributions. In addition for impulsive collisions the details of the lattice dynamics are unimportant for the energy transfer.

An interesting possibility, that cannot simply be excluded, is that the creation of electron–hole pairs gives a substantial contribution to the energy transfer at high incidence energies. This channel is expected to only involve small lateral momentum transfers and should not give a large contribution to the angular distribution. In fact, the enhanced average energy transfer in the measured data around the specular direction is consistent with these channel having small lateral momentum transfers. More substantial support for this mechanism comes from the observation of electron-hole pair creation in hyperthermal scattering of Xe from the semi-conductor surface InP(100) [34]. At an incidence energy of 9 eV, they estimate that about 5% of the energy loss goes into electron-hole pairs. On a metal with no energy gap this channel for energy transfer is expected to be more effective. Obviously, more work is needed to prove or disprove our suggestion that the electron-hole pair channel is responsible for the enhanced values of the measured average energy transfers at high incidence energies.

Finally, we find it instructive to compare some of the features of the scattering dynamics for Ar and Xe from Pt(111). The mass ratio of 0.97 between a Xe atom and a Pt atom is large compared to the corresponding ratio 0.56 for an Ar atom which makes the energy and momentum transfer to the Pt surface much more effective for Xe scattering than Ar scattering from this surface. For instance at $E_{\rm i}$=6.8 eV and $\theta_{\rm i} = 30°$, $\frac{\langle E_{\rm f}\rangle}{E_{\rm i}}$ can be as low as 0.15 for Xe with a $\Delta\theta_{\rm f}$ about 45° while $\frac{\langle E_{\rm f}\rangle}{E_{\rm i}}$ never goes below 0.6 for Ar and $\Delta\theta_{\rm f}$ is only $\sim 25°$. Furthermore, the loop in the in-plane $E_{\rm f}(\theta_{\rm f})$ curve corresponding the impact near bridge site is much more pronunced for Xe than for Ar and gives rise to distinct features in the angular distributions even at temperatures as high as 800K while such features are not observed for Ar. However, the dependence of $\Delta\theta_{\rm f}$ on $E_{\rm i}$ is similiar at 800 K and display the characteristic minima at $E_{\rm i}\cos^2\theta_{\rm i} \sim 1$ eV that separates the thermal scattering regime from the structure scattering regime.

D. Trapping probabilities

A test of the applicability of the empirical PES at thermal incidence energies is provided by making a comparison with trapping probabilities ζ_0 for Ar on Pt(111) measured by Mullins *et al.* [35]. In Fig. 12, this comparison is made at several different angles of incidence and at a surface temperature of 80K using the scaling $E_{\rm i}\cos^{1.5}\theta_i$ for the incidence energy and angle obeyed by the measured trapping data. In view of the uncertainities of ±10% in the absolute values of the measured ζ_0, the agreement between calculated and measured ζ_0 is remarkable. Even the scaling of the calculated ζ_0 is consistent with experiments.

A somewhat surprising result at a low surface temperature, as shown in Fig. 12, is that the calculated ζ_0 extrapolates to a value less than one in the limit of zero incidence energy. This is an effect of the fact that low frequency lattice modes are important in the energy exchange between the Ar atom and the Pt surface at thermal incidence energies which makes it possible even at 80K for the atom to gain energy in the collision with the surface.

The factors that determine the scaling of ζ_0 for a particle in the physisorption well with incidence energy and angle are well understood [17,18,36–38]. At glancing angle of incidence and after the initial collision with the surface, the particle has a relatively high probability to be trapped at the surface with positive energy. The fate of the particle is then determined by the relative importance of losing energy to the lattice vibrations or leaving the surface either by changing the energy of the lateral motion to normal motion by scattering from the surface corrugation or by gaining normal energy from thermally excited lattice vibrations. Deviations from normal energy scaling occurs in situations when the latter two processes are non-negligible. The fact that the calculated ζ_0 as a function of $\theta_{\rm i}$ and $E_{\rm i}$ deviates from normal-energy scaling and is consistent with the observed scaling of ζ_0 shows that the proposed PES is able to describe in a satisfactory way the surface potential corrugation and energy exchange with the lattice vibrations at thermal incidence energies.

Similiar kind of agreements with the measured ζ_0 but with different scalings with $\theta_{\rm i}$ and $E_{\rm i}$ have been obtained by Head-Gordon *et al.* [18] and Smith *et al.* [17] in their molecular dynamics calculations of ζ_0. As discussed in Section III A their potentials have more or less been optimized to describe the interaction of Ar with Pt at thermal energies of incidence while our potential model cover a much wider range of energies. The values for ζ_0 calculated by Head-Gordon *et al.* scale like $E_{\rm i}\cos^{1.75}\theta_i$ and the values calculated by Smith *et al.* obey closely normal energy scaling $E_{\rm i}\cos^2\theta_i$.

V. CONCLUDING REMARKS

An empirical potential energy surface for the Ar/Pt(111) system has been constructed mainly from "inverting" new molecular beam scattering data for this system using classical molecular dynamics. The scattering data for in-plane intensities and average energy transfers over the scattering angle cover a wide and hitherto unexplored range of scattering conditions; incidence energies from 0.06eV to $\sim$7.4 eV, angles from 30° to 60°, and temperatures from 85K to 800K. These data include both the thermal and structure scattering regimes. In addition, we have also made use of experimental data for the well-depth and Ar-Pt(111) stretch frequency and calculated values for the asymptotic van der Waal attraction. The PES consists of a repulsive branch representing the Pauli repulsion between a closed shell atom with the metal surface and an attractive branch representing the van der Waals interaction. Both these two branches are simply modelled by sums of pair potentials with a minimal number of parameters. For the repulsive branch, the pair-potential has to be non-central in order to have a realistic position of the repulsive wall without having too large a surface potential corrugation.

The calculated scattering intensities and average energy transfers over the scattering angle are in satisfactory agreement with the experimental data reported here and the low-energy scattering data measured by Hurst *et. al* [27]. The main discrepancies between theory and experiments occur at the lowest temperature of 85K and intermediate incidence energies for the widths of the angular distributions and at the highest incidence energies for the average energy transfer. The former discrepancy could be corrected by a more complex potential energy function while we argue that the latter discrepancy is not an inadequacy of the proposed potential energy function. We believe instead that the missing energy transfer in the high energy region might be due to creation of electron-hole pair excitations in the metal by the scattered Ar atom. A comparison between calculated and measured trapping probabilities for Ar on Pt at 80K and for different angles of incidence shows that the proposed PES is able to describe in a satisfactory way the surface potential corrugation and energy exchange with the lattice vibrations at thermal incidence energies.

In the future it would be of interest to develop a PES that is able to give a better agreement with the surpringly narrow angular distributions measured at low temperatures and intermediate energies. This development should preferably be based on electronic structure calculations of the forces exerted by the Ar atom on the Pt surface atoms which are now becoming feasible within density functional theory using the local density approximation and a slab representation of the surface.

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TABLES

TABLE I. Deduced potential parameters.

Ar – Pt					
A (eV)	$\alpha(\text{Å}^{-1})$	$h_{\rm r}(\text{Å})$	C_6 (eVÅ^6)	$h_{\rm a}$ (Å)	r_0 (Å)
2.0×10^4	3.3	-0.75	68.15×10^3	0	6.0

FIGURES

FIG. 1. Comparison between calculated and measured angular distributions for scattering of Ar from Pt(111) at different incidence energies and at an incidence angle of 30° with respect to the surface normal. The measured data and calculated results are given by solid and dashed lines, respectively. All results correspond to a surface temperature of 800K.

FIG. 2. Comparison between calculated and measured angular distributions for scattering of Ar from Pt(111) at different incidence energies and at an incidence angle of 45°. Otherwise, same conditions as in Fig. 1.

FIG. 3. Comparison between calculated and measured angular distributions for scattering of Ar from Pt(111) at different incidence energies and at an incidence angle of 60°. Otherwise, same conditions as in Fig. 1.

FIG. 4. Comparison between calculated and measured angular distributions for scattering of Ar from Pt(111) at different surface temperatures. The measured data and calculated results are given by solid and dashed lines, respectively. All results correspond to an incident energy of 0.67 eV and an incidence angle of 45°.

FIG. 5. Comparison between calculated and measured angular distributions for scattering of Ar from Pt(111) at different incidence energies and at a low surface temperature of 85K. The solid and dashed lines are the experimental and calculated results, respectively. All results correspond to an incidence angle of 30°.

FIG. 6. Comparison between calculated and measured average final energies for scattering of Ar from Pt(111) at different incidence energies and at an incidence angle of 30°. The measured data and calculated results are given by symbols and lines, respectively. All results correspond to a surface temperature of 800K. The result expected from lateral momentum conservation, as given in Eq. (4.1), is indicated by the short-dashed line while the result expected from a binary collision, as given in Eq. (4.2), is indicated by the dash-dotted line.

FIG. 7. Comparison between calculated and measured average final energies for scattering of Ar from Pt(111) at different incidence energies and at an incidence angle of 45°. Otherwise, same conditions as in Fig. 6.

FIG. 8. Comparison between calculated and measured average final energies for scattering of Ar from Pt(111) at different incidence energies and at an incidence angle of 60°. Otherwise, same conditions as in Fig. 6.

FIG. 9. Comparison between calculated angular and average final energies for scattering of Ar from Pt(111) with experimental data obtained by Hurst *et al.* [27] at an incidence angle of 45°. Calculated results for average final energies and scattering intensities are given by solid and dashed lines, respectively, while the corresponding experimental results are indicated by solid and open symbols, respectively. The incidence energies and surface temperatures were 0.113 eV and 500K, respectively, in a) and 0.31 eV and 707K, respectively, in b). The expected result for the average energies predicted from lateral momentum conservation, as given in Eq. (4.1), is indicated by the short-dashed line while the corresponding result expected from a binary collision, as given in Eq. (4.2), is indicated by the dash-dotted line.

FIG. 10. Calculated final energy versus scattered angle for in-plane scattering of Ar from Pt(111) at an incidence energy of 7.25 eV and incidence angle of 30°. a) The scattered intensities are shown by solid lines while the final energies are shown by the dotted line and their average by the dashed line, respectively. b) The final energies are shown for three different values for the repulsive potential parameter $\alpha = 3.0\text{Å}^{-1}$ (solid line), 3.3Å^{-1} (dash-dotted line), and 3.6Å^{-1} (dashed line). The results for the final energies expected from a binary collision, as given in Eq. (4.2), are shown by the short-dashed line.

FIG. 11. Calculated final energy versus scattered angle for in-plane scattering of Ar from Pt(111) under the same scattering conditions as in Fig. 10 but for a much more corrugated repulsive branch. The values of the repulsive potential parameters are $A = 16.3 \times 10^4$eV and $\alpha = 6\mathring{A}^{-1}$. The results shown by the short-dashed line are same as in Fig. 10.

FIG. 12. Comparison between calculated and measured trapping probabilities for Ar on a Pt(111) surface at different angles of incidence and at a surface temperature of 80K. The experimental data and their scaling with incident energy are taken from Mullins *et al.* [35]. The calculated and measured probabilities are displayed as open and solid symbols, respectively.