Quasi-harmonic vs. “exact” surface free energies of Al: a systematic study employing a new interatomic potential

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We discuss a computationally efficient classical many-body potential designed to model the Al-Al interaction in a wide range of bonding geometries. We show that the potential yields results in properties in excellent agreement with experiment and ab initio results for a number of bulk and surface properties, among others for surface and step formation energies, and self-diffusion barriers. As an application, free energy calculations are performed for the Al (100) surface by Monte Carlo thermodynamic integration and the quasi-harmonic approximation. Comparison of the latter approximation with the reference Monte Carlo results provides informations on its range of applicability to surface problems at high temperatures.

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I. INTRODUCTION

Atomistic simulations are playing an increasingly prominent role in materials science. From studies of crystallization of clusters to large-scale simulations of fracture and grain boundary diffusion, atomistic simulations offer a microscopic physical view that cannot be obtained from experiment. Predictions resulting from this atomic level understanding are proving increasingly accurate and useful.

The effective interatomic interaction potential is the key ingredient in all atomistic simulation. The accuracy of the potential affects drastically the quality of the simulation result, and its functional complexity determines the amount of computer time required. Much research effort has therefore been devoted to the design of potential energy functions. This is especially important in classical dynamics which, although quantum mechanical simulations have been progressing at a rapid pace in recent years, remains the most (sometimes, the only) affordable way to perform very large scale simulations in materials science. In this paper, we present a new carefully designed Al-Al interaction model, test its performance, and we apply it to the study of free energies in atomic scale simulations.

The ability to compute free energies is essential to understand or predict many physical phenomena, from the stability of crystal structures, to the propensity to form defects or disorder, and to morphology changes and phase transitions. However, the determination of free energies from atomic scale computer simulations is a daunting task. Approximate methods, mostly based on the harmonic vibrational properties of the system, are commonly in use to this end. Here, we compare several possible versions of the so called quasi-harmonic approximation, using as reference accurate simulation using canonical or constant-pressure Monte Carlo methods and thermodynamic integration, focusing on the specific case of surface free energies. The goal is to provide a measure of the range of applicability of approximate methods for complex systems using a reliable Al interaction model.

II. AL INTERACTION POTENTIAL

Previously developed interatomic potentials for the Al-Al interaction have mostly focused on bulk and molecular properties. In this work, we analyze and generalize one of those models with special regard to surface properties, aiming as usual at describing Al in as wide a range of chemical environments as possible, i.e. ranging from bulk Al to Al surfaces and surface steps, and to small Al molecules. The functionalities of the refined potential are found to extend significantly those of previous ones. As we are going to use an embedded atom interaction model, in this Section we briefly review the basic ideas of this approach, describe the details of the model, and finally assess its quality.

A. Theory

In the embedded atom method, each atom in a solid is viewed as an impurity embedded in a host comprising all the other atoms. The energy of the host with impurity is, according to Stott and Zaremba, a functional of the unperturbed host electron density, and a function of the impurity type and position,

\[ E = F_{Z,R}[\rho_h(r)], \]

where \( \rho_h(r) \) is the unperturbed host electron density, and \( Z \) and \( R \) are the type and position of the impurity. Here the energy of an impurity is determined by the electron density of the host before the impurity is added. The functional \( F \) is a universal function, independent of the host, but its form is unknown. A simple approximation...
to $F$ is the so-called local approximation, whereby the
impurity experiences a locally uniform electron density. This
can be viewed as the lowest-order term of an expansion
involving the successive gradients of the density. The
functional $F$ is then approximated by

$$E = F_i(\rho_i(R_i)) + \frac{1}{2} \sum_j \phi_{ij}(R_{ij}), \quad (2)$$

where $\phi_{ij}$ is a pair potential representing the electrostatic
interaction, $R_{ij}$ is the distance between atoms $i$ and $j$, and $F_i$ denotes the embedding energy. The total energy
of the system is a sum over all individual contributions:

$$E_{tot} = \sum_i F_i(\rho_{h,i}) + \frac{1}{2} \sum_{i,j} \phi_{ij}(R_{ij}). \quad (3)$$

A further simplification is introduced assuming that the
host density $\rho_{h,i}$ at atom $i$ is closely approximated by a
sum of the atomic densities $\rho_j$ of the constituent atoms,
\textit{i.e.} $\rho_{h,i} = \sum_{j, (j \neq i)} \rho_j(R_{ij})$, with $\rho_j$ being the contribution to the density at atom $i$ from atom $j$. Equation
(3) is the form commonly used for molecular dynamics
simulations of metals, and is known as embedded atom
potential.

**B. Details of the Al-Al interaction potential**

The Ercolessi-Adams interaction model for Al was con-
structed with the so-called force matching method, and, in contrast to most other empirical models, it gives
excellent structural and elastic properties for the bulk
along with the correct surface interlayer relaxations at
low-index surfaces. Furthermore, we found that the
diffusion barriers for surface adatoms obtained by the
Ercolessi-Adams model are in fair agreement with \textit{ab initio}
calculations \[14\] \[15\] whereas those predicted by most other embedded atom potentials differ drastically \[14\] \[15\] from \textit{ab initio} results. We therefore started off from the
Ercolessi-Adams potential to build our own refined Al–
Al interaction. Without affecting the elastic properties
and the surface relaxation properties, we introduced the
following modifications to the model:

1. An additional term was introduced in the pair
potential $\phi_{ij}$ in order to account for an exponential
Born-Mayer-like repulsion at short Al-Al separation. \[13\] This is a key requirement for studies of \textit{e.g.} physical vapor deposition processes, where the energy of each single atom easily exceeds the thermal energy by as much as three orders of magnitude.

2. In the low density region, three parameters of the
embedding function $F$ were changed in order to im-
prove several reference quantities, namely the Al$_2$
binding energy, and vibrational frequency, and the

3. A fifth-order polynomial cut-off function was intro-
duced, smoothly bringing the potential to zero at an
interatomic distance of 5.56 Å (slightly larger than the third-nearestneighbor distance in bulk Al).

The total energy $E_{tot}$ of a system containing Al atoms
in an arbitrary arrangement is written (see Sec. \[II\] \[A\]) as

$$E_{tot} = \sum_i F(\rho_i) + \frac{1}{2} \sum_{i,j} \overline{\phi}_{ij}(r_{ij}). \quad (4)$$

The atomic density $\rho_i$ in arbitrary units is given as

$$\rho_i = \sum_{j, (j \neq i)} \rho(r_{ij}) \times f_c(r_{ij}, R_0, D_0). \quad (5)$$

The sum runs over all atoms that lie within the potential
range $R_0 + D_0$ (5.56 Å), which is enforced by the cutoff
function $f_c(r, R, D)$. This function is zero for $r$ exceeding
$R + D$ and unity for $r$ less than $R - D$. For $r$ within the
interval $(R - D, R + D)$ it is defined according to

$$f_c(r, R, D) = -3 \left[ \frac{r - R}{D} + 1 \right]^5 + \frac{15}{2} \left[ \frac{r - R}{D} + 1 \right]^4$$
$$-5 \left[ \frac{r - R}{D} + 1 \right]^3 + 1. \quad (6)$$

The function $\rho(r)$ in Eq. (5) is spline-interpolated using the
values reported in Table \[I\]; the parameters $R_0$ and
$D_0$ are given in Table \[I\]. The embedding function $F(\rho)$
is also spline-interpolated, and the corresponding values for $F(\rho)$ are collected in Table \[I\].

The pair potential term in Eq. (5) is written according to

$$\overline{\phi}_{ij} = \left[ \phi(r_{ij}) + (A \exp\{-\lambda r_{ij}\}) \times f_c(r_{ij}, R_0, D_0) \right. \left. -B \right] \times f_c(r_{ij}, R_0, D_0). \quad (7)$$

The function $\phi$ is tabulated in Table \[V\]. The first cut-
off $f_c(r_{ij}, R_0, D_0)$ switches on the exponential repulsive
term at small distances ($r < 2.25$ Å), while $f_c(r_{ij}, R_0, D_0)$
terminates the interaction range of the potential. The
corresponding parameters are given in Table \[I\]. The
exponential term ensures that one gets a Born-Mayer repul-
sion at short separations for, \textit{e.g.}, diatomic molecules. \[13\]

**C. Assessment of the potential**

We now present evidence that the potential just de-
scribed yields satisfactory results for a variety of prop-
erties of Al in different environments. In particular we
address the bulk, the dimer, low-index surfaces and steps
thereon, and self-diffusion on different low-index surfaces;
also included in this test section is the energy dependent sticking coefficient of high energy Al atoms on Al (111). The changes to the potential significantly improved agreement with experiment and other theoretical predictions in several instances where errors were typically of order 50%.

1. Bulk properties

By construction our model does not alter the equilibrium lattice constant \( a_0 \), the cohesive energy \( E_{\text{coh}} \), and the elastic properties of the previous model of Ercolessi. We obtain as in Ref. \[E\] \( a_0 = 4.03 \text{ Å}, E_{\text{coh}} = 3.36 \text{ eV}, C_{11} = 118 \text{ GPa}, C_{12} = 62 \text{ GPa} \) and \( C_{44} = 36 \text{ GPa} \). For comparison, the experimental values are \( C_{11} = 114 \text{ GPa}, C_{12} = 62 \text{ GPa} \) and \( C_{44} = 32 \text{ GPa} \), and LDA calculations predict \( a_0 = 3.98 \text{ Å}, E_{\text{coh}} = 4.15 \text{ eV}, C_{11} = 135 \text{ GPa}, C_{12} = 70 \text{ GPa} \) and \( C_{44} = 35 \text{ GPa} \).

2. Diffusion barriers

Diffusion is central to many physical processes which determine the morphology of surfaces, such as step flow, nucleation, and growth. It is of obvious importance to study diffusion processes theoretically, since direct observations of surface diffusion by means of field ion microscopy (FIM) are limited to a few surfaces due to the response limits of the materials of interest to high voltages. The barriers for single adatom diffusion on Al surfaces calculated by Stumpf and Scheffler using \textit{ab initio} LDA techniques, provide a stringent test for the present empirical Al-Al interaction model. It is generally accepted that diffusion on flat metal surfaces proceeds by either hopping or exchange. In the two following subsections compare the results of the present model for these mechanisms with previous LDA results.

\textit{Hopping Diffusion} – During hopping diffusion the adatom is moving between minima of the potential energy surface, \textit{i.e.} between stable or metastable binding sites. On the (111) surface the stable adsorption sites are the 3-fold fcc and hcp sites; on the (100) surface there is single independent adsorption site, the four-fold hollow; the (110) surface is analogous, with a five-fold site. Hopping diffusion on the (110) surface is intrinsically anisotropic, since it can proceed perpendicular or parallel to the [110]-oriented atomic rows, respectively via the short bridge or long bridge paths. The activation energies for the long and short bridge are labelled \( E_\parallel \) and \( E_\perp \) respectively.

For each surface we performed total energy calculations for the adatom sitting at the adsorption site and at the bridge site. At the latter site the total energy is minimized with respect to distance of the adatom from surface. All other Al positions are fully optimized. The energy difference between adsorption and bridge site is defined to be the activation energy for hopping diffusion.

\section*{3. Surface and step energies}

The surface energy, defined as the difference between the energy of an atom at the surface and in the bulk environment, is usually calculated as

\[ E_{\text{surf}} = \frac{E_{\text{slab}} - N E_{\text{bulk}}}{2A} \]  
\[ E_{\text{atom}} = \frac{E_{\text{slab}} - N E_{\text{bulk}}}{2N_{\text{surf}}} \]

where \( E_{\text{slab}} \) is the total energy of the slab, \( N \) the total number of atoms in the slab, \( N_{\text{surf}} \) the number of atoms on each surface, \( E_{\text{bulk}} \) is the total energy per bulk atom, \( A \) is the area of each free surface of the slab, and the factor \( 1/2 \) accounts for the two free surfaces of the simulation cell; periodic boundary conditions are applied in
the planar directions. These formulas are not problem-
free in general but we have checked that they are in
the cases of interest to us.

We calculated the formation energies for the low index
(111), (100) and (110) Al surfaces with the present Al-
Al interaction model. The comparison of our results to
those obtained in ab initio LDA investigations, given in
Table VI shows that the trends of surface energies of our
Al model are consistent with the ab initio calculations.
We obtain all surface energies about 20% lower than the
LDA surface energies. Keeping in mind the known LDA overestimate of the binding energies (the LDA cohesive
energy of Al, 4.15 eV, overestimate of the binding energies (the LDA cohesive
energy, the step energy can also be expressed per step
length on the vicinal surface. In analogy to the surface
energy, the step energy can be calculated as

$$E_{\text{step}} = d_{s-s}E_{\text{vicinal}} - l_{\text{terrace}}E_{\text{low-index}},$$

(10)

with $d_{s-s}$ the step-step distance, and $l_{\text{terrace}}$ the terrace length on the vicinal surface. In analogy to the surface
energy, the step energy can also be expressed per step
atom.

Although a stepped vicinal surface can be specified by
its corresponding Miller indices, this notation is not very
convenient, as it does not indicate at first sight the ge-
ometrical structure of the surface. Thus we use instead
the notation $[n(h, k, l) \times m(h', k', l')]$ by Lang et al.,
where $(h, k, l)$ and $(h', k', l')$ are the Miller indices of
the terraces and ledges respectively; $n$ gives the number of
atomic rows in the terrace parallel to the step, and $m$
corresponds to the height of the step. In the case of
monoatomic-height steps, $m$ is omitted in this notation.

For the two low index surfaces Al (100) and Al (111),
we calculated the formation energy of different steps. On
Al (100) there exist two monoatomic steps, the close-
packed {111}-facetted and the more open {110}-facetted.
The former belongs to the family of $(1, 1, 2n+1)$-surfaces,
the latter to the family of the $(1, 0, n)$-surfaces.
For the calculation of the step energies we used the
Al(1,1,15) = Al[9(100) × (111)] and the Al(1,0,9) =
Al[9(100) × (110)] surfaces.

On Al(111) there are two types of close-packed steps,
the {111}-facetted and the {100}-facetted. The corre-
sponding vicinal surfaces belong to the $(n, n, n - 2)$
and $(n, n, n + 2)$ families, respectively. We used the
Al(9,9,7) = Al[9(111) × (111)] and the Al(8,8,10) =
Al[9(111) × (100)] surfaces. The geometry of the different
steps on the Al(100) and Al (111) surface is depicted in
Fig. 1. For all these vicinals, the terraces separating the
steps have the same width of 9 atomic rows. We have ver-
ified that step-step repulsion at these inter-step distances
is already in the long-range elastic regime $\sim d_{s-s}$. In
the steps are far enough to extract their formation energy
without an unknown bias from the interstep interaction.

Table VII lists the results for step formation energies,
and compares them to ab initio data. The empirical Al
potential describes the step formation energies for the
two different steps on Al (111) in excellent agreement
with first-principles calculations. More energy is needed
to create steps on the close-packed Al (111) surface than
on the more open Al (100). The open step on the Al
(100) surface has a 20% larger formation energy than
the close-packed step, in agreement with bond cutting
arguments.

4. The Al Dimer

The dimer is a stringent test for an Al-Al interaction
model, since atoms in a dimer experience a very differ-
cent chemical environment compared to bulk or surface
atoms. For Al$_2$, our model yields a binding energy per
atom of 0.70 eV and a bond length of 2.70 Å. The bind-
ing energy was indeed used as input to determine the
model parameters, matching the LDA value of 0.71 eV
($-0.68 \pm 0.03$ eV experimental, Ref. 40). The lowest vi-
brational frequency is calculated to be $\nu = 290$ cm$^{-1}$,
in excellent agreement with the experimental value of
284.2 cm$^{-1}$. The predicted bond length of our model
matches exactly the experimental estimate. Thus, the
present model describes satisfactorily the bonding of Al
in the rather extreme case of the Al$_2$ dimer.

As the understanding of diffusion and growth requires
a knowledge of the binding energies of small aggregates of
adatoms, we also calculated the energy of two Al adatoms
sitting at neighboring fcc sites on an Al (111) surface.
The energy gain with respect to isolated adatoms is 0.50
5. Sticking coefficient for hyperthermal Al atoms

During physical vapor deposition the Al atoms emitted from the sputter source have a non-thermal energy distribution, with kinetic energies exceeding 10 eV. Therefore the sticking coefficient, a key ingredient for a reliable modelling of metal film growth, cannot be assumed to be constant and independent of the particle’s energy as it is typically done. In order to elucidate the dependence of the sticking coefficient on impingement energy, we start our simulations with the incident Al atom placed outside the interaction range of the surface. Its initial kinetic energy is set in the range of 0 to 125 eV, and its starting angle off the surface normal in the range 0° to 60°, which corresponds to typical ionized physical vapor deposition conditions. The trajectories of the incident atom, and of any other atom which may be etched away from the surface upon impact, are monitored until either a certain time span has elapsed, or the outcoming atoms (in the case of reflection or etching) have traveled a distance of 10 Å away from the surface. Analyzing 200 trajectories per incident energy and angle, we collected a statistically significant sample of well-defined adsorption, reflection, and etching events. The relative probability of the sticking coefficient is calculated as the ratio of the number of adsorption events to the total number. The typical statistical error in the reaction probability thus determined is below 5 %. Fig. 2 depicts the sticking coefficient as a function of energy for Al atoms impinging normally on the surface (solid circles) or at an off-normal angle of 40° (open circles).

The sticking probability varies strongly with the incident kinetic energy; the angle to the normal also has a drastic effect. Details of the molecular dynamics calculations are given in Sec. A 2. Further discussion and results on high energy deposition are reported in Ref. 12.

III. APPLICATION: FREE ENERGY CALCULATIONS

In this applicative Section of the paper, we compare surface free energies of Al computed using different levels of quasi-harmonic approximation, and thermodynamic integration via Monte Carlo simulations. The latter effectively functions as “exact” reference for the various harmonic approximations. Before presenting the results, we briefly review the background theory of the different approaches.

A. Theory

Thermodynamic Integration – The free energy cannot be calculated as an ensemble average. The method of thermodynamic integration circumvents this problem starting from the concept of Stockmayer fluid, a fictitious system in which the interparticle interaction potential $U_{\lambda}$ is gradually switched on from a known reference potential $U_h$ to the actual, full interaction potential $U$; the mixing of $U_h$ and $U$ into the effective potential is controlled by a parameter $\lambda$:

$$U_{\lambda} = (1 - \lambda)U_h + \lambda U.$$  \hspace{1cm} (11)

The key relation of the method concerns the derivative of $F$ with respect to $\lambda$:

$$\frac{dF}{d\lambda} = \langle \frac{dU_{\lambda}}{d\lambda} \rangle = \langle U - U_{\lambda} \rangle.$$  \hspace{1cm} (12)

The subscript $\lambda$ means that the average has to be evaluated with the interaction potential $U_{\lambda}$. Integrating the latter equation one arrives at the following expression for the free energy of the system of interest:

$$F_{\lambda=1} = F_{\lambda=0} + \int_{0}^{1} \langle U - U_{\lambda} \rangle d\lambda$$  \hspace{1cm} (13)

The usual choice for the reference system is the Einstein crystal (i.e. a system of non-interacting harmonic oscillators with the interaction potential $U_h = \frac{1}{2}k_B T \sum_i \langle |r_i - r_0|^2 \rangle$), whose free energy is

$$F_{\lambda=0} = -3Nk_BT \ln \left( \frac{T}{\Theta_D} \right),$$  \hspace{1cm} (14)

with $\Theta_D$ the Debye temperature (394 K for Al). The free energy of the real system can thus be obtained at any given temperature by a series of canonical Monte Carlo simulations.
A faster way to obtain the temperature variation of the free energy is to integrate the thermodynamical relation

$$\frac{d}{dT} \left( \frac{F}{T} \right) = -\frac{1}{T^2} \left( \frac{H}{T^2} \right),$$

(15)

from a reference temperature upwards. This requires a simple (e.g.) Monte Carlo ensemble average of the energy for each temperature, and of course a reference value of $F$ from thermodynamic integration.

In summary, the free energy of the system at a reference temperature $T_0$ is determined by the minimum of the free energy, but that of course a reference value of $F$ from thermodynamic integration. Both steps were performed by canonical Metropolis Monte Carlo simulations. As detailed below, thermal expansion is taken into account performing the NVT Monte Carlo calculations at the temperature-dependent lattice constant determined independently by NPT molecular dynamics.

**Quasi-harmonic approach** – A popular approach to free energy calculations is the quasi-harmonic approximation. Thereby, the full interatomic potential is replaced by its quadratic expansion about the atomic equilibrium positions. The system is then equivalent to a collection of harmonic oscillators, and diagonalization of the corresponding dynamical matrix yields the squares of the normal-mode frequencies, i.e. the phonon spectrum. In bulk systems the dynamical matrix is a $3 \times 3$ matrix; for a slab system it is a $3\ell \times 3\ell$ matrix, where $\ell$ is the number of atomic layers in the slab. The dynamical matrix is given by

$$D_{\alpha\beta}(\ell \ell') = \frac{1}{m} \sum_{\nu'} \Phi_{\alpha\beta}(\ell \ell') \exp[\text{i}\mathbf{q}(\mathbf{r}_0 - \mathbf{r}_{\nu'})]$$

(16)

where the force constant matrix $\Phi_{\alpha\beta}(\ell \ell')$ is defined as

$$\Phi_{\alpha\beta}(\ell \ell') = \left( \frac{\partial^2 U}{\partial u_\alpha(\ell) \partial u_\beta(\ell')} \right)_{0}.$$  

(17)

The subscript "0" indicates that the second derivatives are evaluated at the true mean positions of the atoms, with any displacements from the bulk positions (e.g. surface relaxations or reconstructions) taken into account. The equilibrium positions $x_{00}, y_{00}, z_{00}$ of the atoms are given by the vectors $\ell = (\ell_1, \ell_2, \ell_3)$; the $\ell_3$ axis is perpendicular to the surface and the position of an atom within a plane is specified by $\ell_1, \ell_2$, and $\alpha_\ell(\ell)$ describes the $\alpha$ component ($\alpha = x, y, z$) of the position of the $\ell$-th atom from its mean position $x_{00}, y_{00}, z_{00}$.

The phonon spectrum of bulk Al and of Al (100) is displayed in Fig. 3: upper and lower panels respectively (for both calculations supercells comprising 50 layers stacked along (100) have been employed). A variety of surface modes appear in bulk gaps or split off from bulk band edges. These additional modes are the source of the different vibrational free energy of surface systems in comparison to bulk systems. The free energy in this approximation is calculated for lattice and geometrical parameters $\mathbf{a}$ at temperature $T$ as

$$F(\mathbf{a}, T) = E_0(\mathbf{a}) + k_BT \sum_{\mathbf{k},j} \ln \left( \frac{2\sinh \hbar \omega_j(\mathbf{k})}{2k_BT} \right).$$

(18)

The sum runs over all phonon polarizations $j$ and wave vectors $\mathbf{k}$ in the Brillouin zone, with $\omega_j(\mathbf{k})$ the frequency of the corresponding modes. Both the frequencies, and the internal energy $E_0(\mathbf{a})$ of the ideal static lattice, depend on all the lattice and geometrical parameters $\mathbf{a}$. The latter include the bulk lattice constant and, for the surface, the additional geometrical parameters involved in relaxations or reconstructions.

![Fig. 3. Bulk (a) and surface (b) phonon spectra for Al calculated with a 50 layer slab. In (b) the slab has two (100) surfaces, the frequencies are plotted along lines of high symmetry. The corresponding 2d-Brillouin zone is shown in the inset of panel (a).](image)

In a bulk system the forces on each atom are zero by symmetry, independently of $\mathbf{a}$, so that it is strictly correct to neglect the first derivatives in the quadratic expansion of the potential energy. We have verified that the quasi-harmonic approximation does indeed work very well for the bulk even in comparison to thermodynamic integration. For a surface, the situation is different, since the interlayer spacings (especially those of the top surface layers) will change with respect to the bulk, i.e. the surface will generally either contract or expand. The average equilibrium positions of the near-surface layers (the interlayer spacings are relaxed in the case of simple relaxation) are determined by the minimum of the free energy, but that
is, of course, unknown a priori. In addition, the harmonic
expansion is not strictly correct (since the forces, i.e. the
derivatives of the internal potential energy are not zero
at the free energy minimum), which is why one calls this
the quasi-harmonic approximation to begin with. In fact,
it is clear that there are several levels of approximation
possible for the quasi-harmonic approach; here we con-
sider some of those:

1. The computationally simplest way is to optimize
the atomic configuration and calculate the phonons
at zero temperature, and evaluate the free energy
vs. $T$ using those ingredients for all $T$. Within
this approach, the quasi-harmonic approximation
is strictly valid, as we expand the potential energy
function around the equilibrium positions, and the
$T$ dependence enters solely with Eq.(18). In real
systems, of course, both the surface internal en-
ergy and the vibrational contribution to the free
energy will change with $T$, but it is a priori unclear
to what degree this influences the result.

2. Another way to account for the effects of finite tem-
perature is to take the $T = 0$ atomic positions, rescale
their coordinates as a function of the tem-
perature according to the appropriate bulk thermal
expansion coefficient, and recalculate the phonons
(and hence the free energy) for the expanded lat-
tice. This is a hybrid case in which $T$ not only
affects the force constants, but also the surface in-
ternal energy. Of course it is arbitrary to use the
scaled $T=0$ interlayer spacings at non-zero tem-
peratures. Also, it should be kept in mind that
the harmonic approximation is not strictly valid
for the expansion of the potential energy around
non-equilibrium positions.

3. A further possibility is to rescale all the coordi-
nates according to thermal expansion first, and
then re-optimize all atomic positions; the phonons
and the free energy are calculated for that geom-
etry. Here one is consistent with the prerequisites
of the quasi-harmonic expansion, but at the cost of
getting wrong interlayer spacings at the surface.

4. The real thing is of course to minimize the total
free energy with a “self-consistent” adjustment of
the atomic positions of all layers in the slab system,
resulting in the thermodynamic equilibrium con-
figuration of the surface system. In practice, one
starts with the bulk positions rescaled according
to thermal expansion, and then adjusts the inter-
layer spacings of a few near-surface layers to obtain
the minimum of the free energy. The major con-
tribution is generally due to the first two surface
layers, the only having a sizable displacement from
the bulk interlayer spacing. In our calculations, we
therefore changed $d_{12}$ by $\pm 3\%$ and $d_{23}$ by $\pm 2\%$.

B. Results

We now compare the free energy of an Al(100) sur-
fce calculated within the different quasi-harmonic ap-
proaches (1–4) described above, with the results of ther-
modynamic integration; the latter effectively functions as
exact reference since it takes the full potential into ac-
count, hence in particular all anharmonic contributions.
We chose the (100) surface for demonstrative purposes,
as intermediate between the closed packed (111) and the
more open (110) surface.

1. Comparison of different methods

In order to obtain the bulk lattice constant at different
temperatures we first performed zero-pressure molecular
dynamics simulation[1–4] using our Al potential. In the
linear regime the expansion coefficient is $\alpha = 1.64 \times 10^{-5}$
Å/K, the experimental value being $2.36 \times 10^{-5}$ Å/K[3].
Deviations from linearity set in at about 500 K. The
dimensions of the simulation cell with periodic bound-
ary conditions correspond, in all subsequent calculations,
to the bulk lattice constant at the relevant temperature.
The surface free energy calculations imply the evaluation
of the bulk free energy, and of the free energy of a slab
system with two surfaces. The surface free energy is then
determined with Eq.(9).

In Fig.4 we compare the surface free energy calcu-
lated with thermodynamic integration and the quasi-
harmonic approach. All versions of the latter underes-
timate severely the temperature variation of the surface
free energy. This is mainly due to the neglect of anhar-
monicity, which is also responsible for thermal expansion.
A first important result is then that at temperatures
$T \geq \Theta_D$, the harmonic approximation is inappropriate
for Al surfaces.
FIG. 4. Surface free energies for Al (100) calculated with different quasi-harmonic approaches (as discussed in the text) and with the method of thermodynamic integration. Solid line: approach (1), zero-temperature phonons for all temperatures; dotted line: approach (2), positions rescaled according to thermal expansion; dash-dotted line: approach (3), as (2) with re-optimization of atomic positions; crosses: approach (4), minimization of the free energy in the \( \{d_{12}, d_{23}\} \) plane; dashed line: (TI) thermodynamic integration, reference for harmonic approximations. See text for more details.

Note that the failure of the harmonic approximation for the present relatively high-temperature calculations does not affect the successes of this approach at low temperatures, an example being the recent first-principles calculations for Be surfaces. The reason why those results are compatible with ours is clearly that we work well above the Debye temperature of our system (\( \sim 400 \) K), whereas the highest temperature considered in Ref. is 750 K, well below \( \Theta_B \approx 1000 \) K (as extracted from a Debye-Einstein model). Of course, the quasi-harmonic approach will generally fail if applied to systems at sufficiently high temperatures.

To sort out the relative merits of the various levels of harmonic approximation, we focus on the effects of the interlayer spacing \( d_{12} \) (between first and second layer) and \( d_{23} \) (between second and third layer) on the surface energy and on the vibrational contribution to the surface free energy. Essentially this is the fourth level of approximation mentioned earlier. We pick \( T=450 \) K for demonstrative purposes, and expand the lattice accordingly.

Panel (a) in Fig.5 shows the variation of the plain surface energy as a function of the interlayer spacings (expressed in turn in percentage of the bulk interlayer spacing). An increase of the interlayer spacings tends to increase the energy drastically, a decrease to reduce it. The minimum at around \(-3\%\) for both spacings. These fairly unrealistic values result from the optimization of the interlayer spacing for a laterally expanded surface.

The excess surface free energy, i.e. the vibrational contribution is shown in panel (b) of Fig.5. An increase of the interlayer spacings leads to softer force constants and hence to lower frequencies, which yield according to Eq.(18) a more negative value of the surface excess free energy. The dependence on the first spacing is stronger than on the second, although conceptually both spacings would tend to positive infinity (decoupled Al planes) if only the vibrational contribution mattered.

The opposing tendencies of the internal and vibrational contributions tend to compensate; in fact, summing up the plain surface energy and the vibrational contribution, one arrives at the total surface free energy depicted as a function of the interlayer spacings in panel (c) of Fig.5. For the Al (100) surface, the minimum in the free energy corresponds to \( d_{12} = -0.5 \% \) and \( d_{23} = -0.9 \% \), a compromise between the gain of free energy upon outward relaxation, and that in plain surface energy upon inward relaxation.

In approaches (1) and (2) from our above list (force constants from zero-temperature or rescaled zero-temperature positions), the interlayer spacings are \( d_{12} = -1.5 \% \) and \( d_{23} = -1.3 \% \). These are rather close to the minimum of the free energy found by direct minimization in approach (4); indeed, with reference to Fig.4, both approach (1) (solid line) and (2) (dashed line) match rather closely the values of approach (4) (crosses), i.e. of the full
quasi-harmonic calculation. Approach (3) (dash-dotted line), where we rescaled the lattice constant and then re-optimized all atomic positions, fails badly, going astray already near the Debye temperature, and progressively more so for higher temperatures. This is due to the incorrect (free-energy–wise) spacings imposed on the near-surface layers by the minimization of the internal energy. The spacings are found to be \( d_{12} = -3.4\% \) and \( d_{23} = -3.1\% \) at 450 K, and \( d_{12} = -5.8\% \) and \( d_{23} = -5.5\% \) at 900 K. A glance at panel (c) of Fig. 5 reveals that both of these points in the \( \{d_{12}, d_{23}\} \) plane do indeed correspond to free energies very far away from the minimum (especially at the higher temperature).

In conclusion, the most naive and simplest approach of exporting the \( T = 0 \) force constants and surface energy to non-zero temperature does indeed underestimate considerably the temperature variation of the surface free energy with respect to thermodynamic integration, but it gives gives an agreement comparable to, or better than the sophisticated adjustment of the interlayers to find the free energy minimum.

IV. SUMMARY

We have presented a refined Al interatomic potential for classical dynamics and Monte Carlo simulations. We thoroughly tested its functionalities, finding it to be very accurate for a variety of systems. Next, we applied it to evaluating the performance of quasi-harmonic approaches to free energy calculations for surfaces, comparing the latter results with full thermodynamic integration results. For Al surfaces, the quasi-harmonic approximation shows a progressively increasing error for temperatures above \( \Theta_D \). Different levels of quasi-harmonic approximation have been compared; for Al, the simplest method of using zero-temperature phonons to compute the free energy at all temperatures is as accurate as the explicit minimization of the free energy with respect to geometrical parameters.

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APPENDIX A: COMPUTATIONAL DETAILS

1. Substrate sizes

For the calculation of the surface self-diffusion barriers, and surface and step energies, we have employed finite slabs with periodic boundary conditions for the lateral cells. The supercells contained of 672, 550 and 560 atoms for the Al(111), Al(100) and Al(110) surfaces and consisted of 12, 11 and 9 atomic layers. In order to determine the surface energies of Al(111), Al(100) and Al(110) the supercells contained 1080, 550 and 560 atoms, arranged in 9, 11 and 16 atomic layers. The step formation energies were obtained from systems containing 4 steps and 72, 105, 102 and 102 atoms per layer corresponding to a total number of 1312, 2724, 1368 and 2532 atoms for the Al(1, 0, 9), Al(1, 1, 15), Al(8, 8, 10) and Al(9, 9, 7) surface. All forces \( \mathbf{F} \) per atom have been brought below a threshold of \( 10^{-5} \) eV/Å. We estimated the errors in the total energies due to the finite supercell size to be well below \( 10^{-4} \) eV/atom.

2. Molecular dynamics calculation of the sticking probability

The reaction probabilities were calculated in classical molecular dynamics simulations using our Al interaction potential. The integration was performed with a 5-th order Runge Kutta method with an adaptive timestep, in order to ensure total energy conservation throughout the simulation. Supercells containing 1320 atoms arranged in 10 atomic layers were employed; cell dimensions are chosen so as to avoid artifacts of the in-plane periodicity. The starting configuration is chosen to be a (111) surface, the one Al surface with the lowest formation energy. All atomic coordinates are allowed to evolve dynamically, except those of the two bottom layers of the supercell. The surface temperature is set at 450 K (i.e about 1/2 of the melting temperature, and \( \sim 15\% \) larger than the bulk Debye temperature).

3. Monte Carlo calculations within the canonical ensemble

All Monte Carlo calculations were be performed within the canonical ensemble, using the standard Metropolis technique. The maximum atomic displacement was automatically adjusted in order to get an acceptance ratio of 0.4. It was not systematically studied that this acceptance ratio was an optimum, but well converged statistical averages were obtained with a typical number of Monte Carlo moves of order \( 10^4 \) times the number of atoms in the system. Before averaging, the system was equilibrated for a number of steps of order 500 times the number of atoms in the system. For the Al (100) surface we used in total 384 atoms.
4. Quasi-Harmonic free energy calculations

Within the quasi-harmonic methods we employed slab geometries with 20 atomic layers each containing 32 atoms. For the \( k \)-space summation we used grids typically containing 2500 equally spaced \( k \)-points. Careful tests showed that this number of \( k \)-points yields well converged results.

TABLE I. Parameters used to define the atomic density function \( \varphi(r) \). The positions of the spline knots and the values at the knots are given. Also the first derivatives at the first and last knots are given.
TABLE II. Parameters entering the potential energy function from Eq. (4)

| Parameter | \( R_0 \) [Å] | \( D_0 \) [Å] | \( R_\Phi \) [Å] | \( D_\Phi \) [Å] | \( \Lambda \) [eV] | \( \lambda \) [1/Å] | \( B \) [eV] |
|-----------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Value     | 5.46          | 0.10          | 2.00          | 0.25          | 7255.44       | 4.42085       | 1.04897       |

TABLE III. Parameters used to define the embedding function \( F(\rho) \). The positions of the spline knots and the values at the knots are given. Also the first derivatives at the first and last knots are given.

| \( \rho \) | \( F(\rho) \) [eV] | \( u'(\rho) \) [1/eV] |
|-----------|-----------------|-----------------|
| 0.0       | 0.0000          | -12.375         |
| 0.1       | -0.8139         |                 |
| 0.2       | -1.2697         |                 |
| 0.3       | -1.6799         |                 |
| 0.4       | -2.0296         |                 |
| 0.5       | -2.2520         |                 |
| 0.6       | -2.4272         |                 |
| 0.7       | -2.5517         |                 |
| 0.8       | -2.6052         |                 |
| 0.9       | -2.6440         |                 |
| 1.0       | -2.6571         |                 |
| 1.1       | -2.6456         |                 |
| 1.2       | -2.6087         |                 |
| 1.4       | -2.4525         | 1.0620          |

TABLE IV. Parameters used to define the pair potential \( \phi(r) \). The positions of the spline knots and the values at the knots are given. Also the first derivatives at the first and last knots are given.

| \( r \) [Å] | \( \phi(r) \) [eV] | \( \phi'(r) \) [eV/Å] |
|-------------|-----------------|-----------------|
| 2.0211      | 6.8272×10\(^{-1}\) |                 |
| 2.2737      | -1.8818×10\(^{-2}\) |                 |
| 2.5263      | -5.6801×10\(^{-2}\) |                 |
| 2.7790      | -3.7373×10\(^{-2}\) |                 |
| 3.0317      | -5.1335×10\(^{-2}\) |                 |
| 3.2843      | -6.3286×10\(^{-2}\) |                 |
| 3.5370      | -5.4810×10\(^{-2}\) |                 |
| 3.8066      | -3.7288×10\(^{-2}\) |                 |
| 4.0422      | -1.8887×10\(^{-2}\) |                 |

TABLE V. Comparison of selected hopping and exchange diffusion barriers on low-index Al surfaces obtained with the present model and in \textit{ab initio} calculations. Al (111) is also included for completeness.

| System | This work | \textit{ab initio} |
|--------|-----------|--------------------|
| Al (111) hopping | 0.04 | 0.04\(^a\) |
| Al (100) hopping | 0.60 | 0.68\(^b\), 0.65\(^b\) |
| Al (100) exchange | 0.50 | 0.35\(^a\) |
| Al (110) \(\perp\) hopping | 1.13 | 1.06\(^a\) |
| Al (110) \(\parallel\) hopping | 0.30 | 0.60\(^a\) |

\(^a\)Reference 15; \(^b\)Reference 28

TABLE VI. Surface formation energies for low index Al surfaces calculated with the present model and with other theories.

| System | This work | LDA\(^a\) |
|--------|-----------|-----------|
| Al(111) | 0.38 0.054 0.48 0.070 |
| Al(100) | 0.48 0.059 0.56 0.071 |
| Al(110) | 0.74 0.065 0.89 0.080 |

\(^a\)Reference 17

TABLE VII. Step formation energies for low index Al surfaces calculated with the present model and with other theories.

| System | This work | LDA\(^a\) |
|--------|-----------|-----------|
| Al(100) \(\times\) (111) | 0.055 0.142 |
| Al(100) \(\times\) (110) | 0.066 0.240 |
| Al(111) \(\times\) (111) | 0.083 0.215 0.082 0.232 |
| Al(111) \(\times\) (100) | 0.085 0.222 0.088 0.248 |

\(^a\)Reference 16
