Helium and Argon Interactions with Gold Surfaces: Ab Initio-Assisted Determination of the He–Au Pairwise Potential and Its Application to Accommodation Coefficient Determination

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S Supporting Information

ABSTRACT: Global potentials for the extremely weak interaction between the He atom and gold surfaces are determined from ab initio calculations and validated with experimental-based determinations of well depth values. Dispersionless density functional periodic calculations are combined with effective pairwise functional parameters for the dispersion. These parameters are obtained from time-dependent density functional theory response theory using localized Hartree–Fock orbitals, as applied on He–Au_n clusters. This He–Au pairwise potential is used in molecular dynamics simulations of gas–gold surface collisions from which incident and reflected gas atom velocities allow the determination of energy and momentum accommodation coefficients. Boundary quantities such as slip velocity and thermal resistance are not only derived from these coefficients, but also from a new methodology based on a nonparametric kernel, avoiding the atomic description of the gold surface. Similar collision simulations are performed for Ar for comparison. A model of a rough gold surface is also investigated.

1. INTRODUCTION

In the domain of micro-electro-mechanical systems (MEMS), the study of fluid microflows is essential. Slippage and thermal resistance quantities are fundamental to characterize such microflows and are dependent on the fluid and microchannel surface nature. Helium and argon are the usual gases for experimental studies. Gold is also a common coating of MEMS channel surfaces because it is a soft material which presents a strong resistance to oxidation and a reasonably high thermal conductivity. As an illustrative example, Hadj Nacer et al.^{1,2} have experimentally studied the flow of different gases (helium, argon, carbon dioxide, and nitrogen) through microtubes with different coatings, including gold, to obtain accommodation coefficients.

The tangential momentum accommodation coefficient (TMAC) is an interesting quantity allowing the characterization of a fluid–surface interface. It is usually employed in fluid mechanics to evaluate the slip length of the fluid speed at the interface. Depending on its value (comprised in between 0 and 1), the collision of the fluid particles on the surface is characterized as being diffusive (TMAC = 1) or specular (TMAC = 0). The first definition of this parameter was established by Maxwell.³ Many years ago, several methodologies based on molecular dynamics (MD) simulations have been developed to evaluate the value of this parameter from particle velocities and different works have been devoted to determine these coefficients,^{4–8} as well as the so-named energy

accommodation coefficient (EAC). The latter can be used to evaluate the temperature jump at a surface and in some models it is connected to all the momentum accommodation coefficients (MAC).⁸ The present work presents MAC and EAC values, as obtained from the method proposed by Spijker et al.⁹ This method is based on the fit of impacting and reflected velocities of the gas atoms on the solid wall. In this work, this treatment has been applied to both He and Ar atoms to demonstrate the effect of the interaction potential and atomic masses. The effect of the roughness of the solid wall has also been explored. To be more general and to provide useful quantities for Navier–Stokes-based macroscopic flow simulations, interface coefficients such as slippage and thermal resistance parameters have been derived from gas velocities, and from MAC and EAC for comparison. Our new nonparametric (NP) kernel approach has also been applied to verify its efficiency with the peculiar case of helium gas. This approach avoids a full atomic description of the surface without losing its specificity since it is not restricted to the use of just a few parameters.¹⁰

Contrary to most of the works on MAC and EAC determinations, using Lorentz–Berthelot rules for the Lennard-Jones parameters, we use ab initio potentials.

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Following our theoretical work on the interface properties of argon with gold,¹¹ we propose to extend the present study to the helium–gold couple. Helium is the lightest rare gas atom. It has special physical and chemical properties due to its reduced size and weight, compared with heavier rare gases. Then, a peculiar behavior is expected for the interface of helium on gold. The present work addresses both an ab initio-assisted determination of He–Au pair potential and its employment in MD simulations for the determination of interface coefficients of the helium fluid interacting with gold surfaces. The results will also be compared with those obtained for the Ar–Au couple.

In a previous work, the Ar–Au pair potential was derived from calculations on the Ar + Au₂ complex mixing dispersionless density functional theory (dIDF) and a density functional theory (DFT)-based determination of dispersion coefficients (D_{as})¹¹ using symmetry-adapted perturbation theory (SAPT). The He–Au interaction is much weaker than the Ar–Au interaction. The best estimate of the well depth value of the He–Au diatomic molecule is 1.897 meV from the state-of-the-art ab initio calculations.¹² The previous empirical potentials based on the works of Zaremba and Kohn¹³ indicate that the adsorption energy of a helium atom on a Au(111) surface might be about 10 meV^{14–17} with a wide range of values for the equilibrium geometry values, i.e., from 2.5 to 3.98 Å. The best experimental estimate of the well depth was reported in a review by Vidali et al.,¹⁶ being 7.67 meV from scattering measurements. These energy values are an order of magnitude smaller than the Ar–Au(111) ones.¹¹ In the present work, a new strategy based on the dIDF + D_{as} approach is proposed to produce an accurate He–Au pairwise potential.

The present work is organized as follows: in the next section, we describe the derivation of the He–Au pairwise potential from ab initio determinations and the application of the He–Au and Ar–Au potentials in molecular dynamics simulations of gas atom–gold surface collisions. EAC and MAC parameters, and boundary quantities are then derived from the gas velocities. Next, in Section 3, we present the results and especially, the comparison between Ar and He concerning the interaction potentials with gold and the interface quantities. Finally, the main conclusions are provided in Section 4.

2. METHODS

2.1. Helium/Au(111) Interaction Energies: the Periodic dIDF + D_{as}^* Approach. The present section is devoted to the ab initio-assisted determination of He–Au pairwise potential. In the first step, He–Au(111) interaction potential has been computed using the dIDF + D_{as}^* approach, from where the pairwise potential coefficients have been obtained, so that the He–Au potential has the form

$$E_{\text{int}}(R) = \left(A + BR + \frac{C}{R} \right) e^{(-\alpha R - \gamma R^2)} + \sum_{n=6,8} \frac{\sqrt{C_n^{\text{He}} C_n^{\text{Au}}}}{R^n} f_n(\sqrt{\beta_{\text{He}} \beta_{\text{Au}}} R) \quad (1)$$

where R is the distance between a helium atom and a gold atom, A , B , C , α , and γ are the parameters associated with the dispersionless part of the potential, the other parameters concern the dispersion part of the potential, and f_n is the damping function of Tang and Toennies¹⁸

$$f_n(\beta R) = 1 - e^{-\beta R} \left(1 + \beta R + \dots + \frac{(\beta R)^n}{n!} \right) \quad (2)$$

Our approach can be viewed as a complementary extended version of the dispersionless density functional (dIDF) + D_{as} treatment proposed by Pernal et al.,¹⁹ with D_{as} being a general-purpose effective pairwise functional for the dispersion.^{19–21} The idea underlying the scheme (denoted then as the periodic dIDF + incremental D_{as}^* approach²²) is the partition of the global interaction energy into dispersionless as well as dispersion contributions. The dispersionless contribution is obtained through the periodic dispersionless dIDF approach.²² Next, dispersion contributions are calculated via time-dependent density functional response theory, using the localized Hartree–Fock method,²³ on a Au₁₀ or Au₄ surface cluster model, allowing the D_{as} function parametrization (denoted as D_{as}^* parametrization). The D_{as}^* function is then employed to extrapolate the adsorbate/cluster dispersion contribution to the extended adsorbate/surface system.

As mentioned above, our pairwise potential model uses different functions for the dispersionless and dispersion energy contributions. It accounts for the typical exponential growth of the dominant dispersionless contribution, the exchange-repulsion, including a Gaussian-type “cushion” to describe weakly attractive tails stemming from other dispersionless terms

$$E_{\text{int}}^{\text{disp-less}}(\{\mathbf{R}_{\text{He-Au}}\}) = \sum_{\text{Au}} \left(A + BR_{\text{He-Au}} + \frac{C}{R_{\text{He-Au}}} \right) e^{(-\alpha R_{\text{He-Au}} - \gamma R_{\text{He-Au}}^2)} \quad (3)$$

where $R_{\text{He-Au}}$ stands for the distance between the adsorbate and one gold atom of the surface. The sum in the second term runs over all the gold atoms of the surface. For the dispersion part, the D_{as}^* function has the typical C_6/C_8 expansion with the damping functions of Tang and Toennies f_n ($n = 6, 8$)¹⁸

$$E_{\text{int}}^{\text{disp}}(\{\mathbf{R}_{\text{He-Au}}\}) = - \sum_{\text{Au}} \sum_{n=6,8} \frac{\sqrt{C_n^{\text{He}} C_n^{\text{Au}}}}{R_{\text{He-Au}}^n} f_n(\sqrt{\beta_{\text{He}} \beta_{\text{Au}}} R_{\text{He-Au}}) \quad (4)$$

where the Au sum applies on all the gold atoms of the Au₄ or Au₁₀ cluster.

It has been found that an appropriate tuning of dispersion model parameters is achieved using rather small cluster models composed of four and ten gold atoms (see Section 3.1). In fact, one basic conclusion from the accurate studies of van der Waals-dominated adsorbate/surface systems (see e.g., refs 24, 25) is that, although the dispersion is long-range, dispersion parameters show excellent transferability properties upon increasing the size of the surface cluster models.

For comparison purposes, a vdW-corrected DFT-based treatment has also been applied for the determination of the He–Au(111) interaction potential. Specifically, within the framework of the nonlocal vdW density functionals developed by Langreth and co-workers, we have chosen the second-generation vdW-DF2 treatment.²⁶

The details concerning all the electronic structure calculations can be found in the Supporting Information (SI).

2.2. Momentum and Energy Accommodation Coefficients, Slippage and Temperature Jump. The MAC

coefficient α_k and the EAC coefficient α_e are defined by the relations²⁷

$$\alpha_k = \frac{\langle c'_k \rangle - \langle c_k \rangle}{\langle c'_k \rangle - \langle c_{wk} \rangle}, \quad \alpha_e = \frac{\langle c'^2 \rangle - \langle c^2 \rangle}{\langle c'^2 \rangle - \langle c_w^2 \rangle}, \quad k = x, y, z \quad (5)$$

where c'_k , c_k , and c_{wk} are the k -components of the incident, reflected and wall-thermalized gas atom velocities, respectively. The latter is drawn from the equilibrium distribution at the wall temperature T_w . The notation $\langle \rangle$ stands for the average over the number of collisions, or equivalently the number of molecules crossing a control plane parallel to the wall. Since $\langle c_{wk} \rangle$ and $\langle c_w^2 \rangle$ can be computed from the equilibrium distribution, they are known quantities as a function of T_w . The calculation of $\langle c'_k \rangle$ and $\langle c_k \rangle$ depends on their distributions or on the choice of incident velocities c'_k and the associated reflected velocities c_k . If α is close to 1, the collisions are characterized as being diffusive and if α is close to 0, they are characterized as being specular instead. Theoretically, the accommodation coefficients are related to the slip and jump coefficients via the expressions

$$\beta_{1k} = \frac{\alpha_k}{2 - \alpha_k}, \quad \beta_2 = \frac{\alpha_e}{2 - \alpha_e}, \quad k = x, y \quad (6)$$

where β_{1k} is the dimensionless Navier tangential friction coefficient, depending on tangential accommodation coefficients α_k , and β_2 is the dimensionless temperature resistance coefficient or Kapitza coefficient, depending on the energy accommodation coefficient α_e . These coefficients appear in the following sets of boundary conditions for Navier–Stokes–Fourier equations

$$\beta_{1k} v_k = -\frac{\sigma_{kz}}{n} \sqrt{\frac{\pi}{2k_B T m_g}}, \quad \beta_2 (T - T_w) = -\frac{q_z}{n} \sqrt{\frac{m_g \pi}{8k_B^3 T}}, \quad k = x, y \quad (7)$$

where m_g is the mass of the gas atom, T is the average temperature near the wall, and k_B is the Boltzmann constant. As can be observed from eq 7, when the number density n and temperature T are kept fixed, the slip velocity v_k is proportional to the shear component of the pressure tensor σ_{kz} and the temperature jump $T - T_w$ is proportional to the normal heat flux component q_z .

In an ideal case, the accommodation coefficients are constant and can be determined by eq 5. Specifically, we can beam independently gas atoms onto the solid surface and average incident and reflected velocities to calculate MAC and EAC values. When the incident velocity set has the same mean velocity and temperature as the wall, the zero denominator is susceptible to numerical issues. In this case, Spijker et al.⁹ proposed to analyze the correlation between the input (incident) and output (reflection) data. In practice, it consists of computing the best least-square linear fit of all (c'_k, c_k) points obtained after a large number of collisions

$$\alpha_k = 1 - \frac{\sum (c'_k - \langle c'_k \rangle)(c_k - \langle c_k \rangle)}{\sum (c'_k - \langle c'_k \rangle)^2}, \quad k = x, y, z$$

$$\alpha_e = 1 - \frac{\sum (c'^2 - \langle c'^2 \rangle)(c^2 - \langle c^2 \rangle)}{\sum (c'^2 - \langle c'^2 \rangle)^2} \quad (8)$$

For realistic surfaces, however, the accommodation coefficients might not be constant and cannot be used to model the gas–wall interaction. In this case, Liao et al.¹⁰ proposed to use a

nonparametric approach to construct the relationship between the incident and the reflected velocity distributions. From the given collision data obtained from MD simulations, it is possible to construct a NP scattering kernel $B(c|c')$

$$B(c|c') = P(c|c') = \prod_k B_k(c_k|c'_k), \quad k = x, y, z \quad (9)$$

where c'_k and c_k are the incident and reflective velocity components, respectively. Here, $B(c|c')$ is the usual conditional probability density $P(c|c')$ of c for given c' and is decomposed in three independent realizations $B_k(c_k|c'_k)$ depending on directions $k = x, y, z$, respectively. By (eq 9), we assume that the reflective velocity component depends only on the incident velocity component of the same direction and neglect the influence of the incident velocity component associated with different directions. Such decomposition avoids the curse of dimensionality, easing the construction of the kernel $B(c|c')$ from the available collision data. Using the NP kernel, we can generate new velocity data, i.e., generating a random output c_k for a given input c'_k . This kernel can serve to set boundary conditions in the Boltzmann equation and particle-based simulation methods, including direct simulation Monte Carlo and MD treatments.

It is also possible to directly determine the boundary coefficients for Navier–Stokes–Fourier equations β_{1k} , β_2 without using intermediate accommodation coefficients. It is sufficient to use suitable input velocities, for example, nonequilibrium gas velocity distribution. Usually, to identify β_{1k} , we use the distribution with the same temperature as the wall, but with different mean tangential velocity. To compute β_2 , the input distribution has zero mean tangential velocity but different temperatures are used. Output velocities can be generated via the fast NP scattering kernel or via realistic but more time-consuming collisions with the atomic wall. From the two input and output distributions, the stream velocity v_k and temperature T can be computed as

$$v_k = \frac{\langle c_k/|c_z| + c'_k/|c'_z| \rangle}{\langle 1/|c_z| + 1/|c'_z| \rangle}, \quad T = \frac{m_g \langle c^2/|c_z| + c'^2/|c'_z| \rangle}{3k_B \langle 1/|c_z| + 1/|c'_z| \rangle} \quad (10)$$

and the heat flux $-q_z/n$ and shear stress $-\sigma_{kz}/n$ as

$$-\frac{\sigma_{kz}}{n} = \frac{m_g \langle c'_k - c_k \rangle}{\langle 1/|c_z| + 1/|c'_z| \rangle}, \quad -\frac{q_z}{n} = \frac{m_g \langle c'^2/2 - c^2/2 \rangle}{\langle 1/|c_z| + 1/|c'_z| \rangle} \quad (11)$$

and use them to calculate the interface coefficients. The above expressions are obtained from the consideration of MD collision simulations and the kinetic theory where physical quantities are moments of phase density functions. To simplify the calculation, we normalized the values in eqs 10 and 11 as follows

$$\hat{\sigma}_{kz} = \frac{\sigma_{kz}}{nm_g \zeta^2}, \quad \hat{v}_k = \frac{v_k}{\zeta}, \quad \hat{q}_z = \frac{q_z}{2nm_g \zeta^3},$$

$$\Delta \hat{\theta} = \frac{k_B (T - T_w)}{m_g \zeta^2}, \quad \zeta = \sqrt{\frac{2k_B T}{m_g \pi}} \quad (12)$$

So, the slip and jump coefficients are rewritten as

$$\beta_{1k} = \frac{-\hat{\sigma}_{kz}}{\hat{v}_k}, \quad \beta_2 = \frac{-\hat{q}_z}{\Delta \hat{\theta}}, \quad k = x, y \quad (13)$$

Figure 1. Cloud figures of incident (horizontal axis) and reflected (vertical axis) velocity components of 100 000 collisions of He and Ar atoms at 300 K projected on smooth and rough Au surfaces at 300 K. The horizontal dashed lines correspond to the full diffusive case, the diagonal ones to the full specular case. The red lines correspond to the linear fit of the velocity cloud. The corresponding MAC and EAC values are given in Table 1.

Table 1. MAC and EAC Results for He and Ar Collisions on Smooth and Rough Au Surfaces at 300 K^a

gas	surface	T_g (K)	α_x	α_y	α_z	α_e	T_{in} (K)	T_{out} (K)
He	smooth	100	0.007	0.007	0.144	0.038	99.844	104.698
		200	0.010	0.010	0.073	0.023	199.693	201.602
		300	0.011	0.012	0.049	0.018	299.536	299.712
		400	0.016	0.016	0.043	0.020	399.390	397.231
	rough	100	0.380	0.341	0.354	0.044	99.844	105.727
		200	0.347	0.320	0.309	0.025	199.696	202.202
		300	0.341	0.311	0.294	0.025	299.536	299.430
		400	0.336	0.286	0.273	0.025	399.381	396.747
Ar	smooth	100	0.524	0.536	0.940	0.763	99.845	234.667
		200	0.478	0.476	0.864	0.676	199.689	261.217
		300	0.427	0.423	0.801	0.597	299.531	298.060
		400	0.385	0.391	0.748	0.531	399.383	341.999
	rough	100	0.792	0.785	0.951	0.800	99.845	243.593
		200	0.734	0.726	0.888	0.721	199.691	265.816
		300	0.691	0.683	0.829	0.632	299.535	299.214
		400	0.661	0.648	0.784	0.560	399.388	339.517

^a T_g is the temperature defining the incident velocity distribution of the gas atom (see SI). T_{in} and T_{out} are defined by eq 14.

In what follows, the different methods briefly described above will be applied to study the accommodation coefficients and the slip/jump coefficients.

The gas atom velocities were obtained from molecular dynamics simulations of collisions of He or Ar on a gold surface, using the He–Au, Ar–He pairwise potentials derived

above and in ref 11, respectively. The technical details are given in the Supporting Information. After each collision, the atomic velocity components are collected such that α_k is derived from the least squares linear fit of the clouds of points (c'_k, c_k) ⁹ (see eq 8). Each sum is over all the collisions. Some velocity clouds are shown in Figure 1 for He or Ar colliding on gold surfaces.

Figure 2. Smooth Au (left) and rough (right) surfaces of gold. Eight hundred yellow atoms are originated from the initial smooth surface. Ninety-six blue atoms were deposited to form the rough surface composed of 896 atoms.

Figure 3. Radial scan of the interaction energies between atomic helium and the Au(111) surface, with the helium atom located at fcc (left panel) and top (right panel) positions. The interaction energies obtained with the periodic dlDF + D_{as}^* approach are compared with those determined via the vdW-DF2 scheme. The experimentally based value of the well depth, 7.67 meV, is also indicated (gray dashed line).¹⁶

We examine the dependences of α_k with both the gas temperature and the nature of the rare gas atom. The gas temperature was computed from the average of the kinetic energies of the gas atoms before (T_{in}) and after the collision (T_{out}) with the gold surface at 300 K

$$T_{\text{in}} = \frac{\langle c^2 \rangle m_g}{4k_B}, \quad T_{\text{out}} = \frac{\langle c'^2 \rangle m_g}{4k_B} \quad (14)$$

The resulting MAC and EAC values are presented in Table 1.

To investigate the effect of the roughness of the surface on the MAC and EAC values, a rough surface was created by projecting gold atoms on the Au(111) surface (see SI). A surface example is illustrated in Figure 2 for which 96 Au atoms have been trapped after projection. The corresponding MAC and EAC values for different gas temperatures are given in Table 1.

In the NP model, we delimited the He velocity range from -4 to 4 nm/ps, and the Ar velocity range from -2 to 2 nm/ps. These ranges cover over 99.999% the gas velocities at 300 K. We used the kernel density estimation to estimate the joint probability density of velocities from existing collision data (Figure 1) and to generate the random reflection velocity for a given incident velocity. For that, we discretized the incident velocity space into 100 intervals and the reflective velocity space into 1000 intervals. Next, we took a bandwidth of 0.2 nm/ps and used the Parzen-window method to calculate the numerical cumulative distribution function of the reflective

velocities under different incident velocities. The probability of a reflective velocity not belonging to a category was determined by interpolation.

3. RESULTS AND DISCUSSION

3.1. Helium/Au(111) Interaction Energies. The interaction energies obtained with our potential model (referred to as dlDF + D_{as}^*) are compared to those determined via the vdW-DF2 scheme in Figure 3. Dispersionless energies obtained from periodic dlDF calculations are indicated with green points, whereas those obtained from the pairwise potential model are indicated with green lines. Total interaction energies obtained using the Au_4 cluster model to tune the dispersion parameters are compared with those obtained using the Au_{10} cluster model. The experimentally based value of the well depth is also indicated (gray dashed line). As shown in Figure 3 and Table 2, the well depth values calculated with the dlDF + D_{as}^* treatment are very close to those based on experimental measurements.¹⁶ It can also be seen that the vdW-DF2 approach²⁶ provides well depth values twice as large. The reason for this overestimation can be understood from the previous studies on He–surface interactions (e.g., see refs 22, 24, 25). Semi-local DFT treatments tend to provide short-range dispersionless contributions which are attractive, whereas the benchmarking at coupled-cluster level indicates that short-range intra-monomer correlation contributions are repulsive. Concerning the equilibrium geometry, compared with the wide range of values

Table 2. Equilibrium Geometries and Well Depths of the Global Interaction Potentials of He with Au(111) for the Face-Centered Cubic (fcc) and Top Adsorption Sites Presented in Figure 3

site	method	R_e (Å)	V_e (meV)
top	vdW-DF2	3.6205	−17.674
	dIDF + D_{as}^* (Au ₄)	4.3519	−7.770
	dIDF + D_{as}^* (Au ₁₀)	4.4124	−7.102
fcc	vdW-DF2	3.6193	−17.619
	dIDF + D_{as}^* (Au ₄)	4.3410	−8.360
	dIDF + D_{as}^* (Au ₁₀)	4.3994	−7.701

reported in the literature (i.e., from 2.5 to 3.98 Å^{14–17}), the dIDF + D_{as}^* approach might produce an overestimated value.

The total interaction energies presented in Figure 3 and the data of Table 2 indicate that the D_{as}^* parametrization obtained from the Au₁₀ cluster model provides dispersion energies which are very close to those using the Au₄ cluster instead (to within about 1 meV for the total energy). The particular position of the He atom in the Au_n clusters, considering both top or fcc positions, was found to be almost irrelevant for the D_{as}^* function parametrization (to within about 0.6 meV for the Au₁₀ cluster case). However, the fcc site provides the most stable minimum using the dIDF + D_{as}^* approach, and the corresponding parameters derived from the Au₁₀ cluster results were used for the definition of the pairwise potential needed for the MD calculations.

Figure 3 results confirm that the He–surface interaction is a special case for which “standard” DFT methods such as vdW-DF2 cannot be used, contrary to the results we obtained for Ar.¹¹ The current version of the dIDF + D_{as}^* approach is a cost-efficient alternative. At a variance with our previous work on the Ar/gold interaction,¹¹ the dispersionless pairwise potential has been obtained from periodic calculations, whereas the dispersion has been determined from TD-DFT linear response theory, using localized Hartree–Fock orbitals, instead of SAPT(DFT) calculations.

The D_{as}^* and dispersionless He–Au coefficients are presented in Tables S2 and S1 of SI, respectively. For comparison and further need, the corresponding Ar–Au coefficients are also included. These parameters provide a pairwise potential well depth value of 0.78723 meV and an equilibrium geometry of 4.8720 Å for the He–Au pair. These values can be compared with those determined for the Ar–Au pair: 11.360 meV and 4.2848 Å, respectively.¹¹ As expected, from the very different polarizabilities of He and Ar atoms, the He–Au D_{as}^* parameters render an interaction which is much less attractive than the Ar–Au interaction. The fact that the dispersionless part has to be expressed by more parameters in the He–Au case also indicates the difficulty to accurately reproduce such an interaction.

3.2. Momentum and Energy Accommodation Coefficients, Slippage and Temperature Jump. The first inspection of Table 1 indicates that the MAC values are, at least, an order of magnitude lower for He than for Ar. The collisions of He on gold are then much more specular than the Ar ones. This result is expected from the difference of pairwise potentials as well as the mass difference between He and Ar.

For both atomic species, α_x and α_y values are almost identical as expected from the study of a smooth isotropic surface. Contrary to the general behavior, α_x and α_y increase with T_g for He colliding with the smooth gold surface, whereas α_z for He and all α component values for Ar decrease with T_g . However, this result may not be significant since α_x and α_y values for He are smaller than 0.02. The roughness increases the $\alpha_{x,y}$ values for both He and Ar gases, indicating that the collisions are more diffusive than with a smooth surface. However, the collisions of He are always more specular than those of Ar in any situation, as confirmed by the results presented in Figure 1. Due to the smaller size of the He atoms, the effect of the surface roughness is more important for He than for Ar. The rough surface has no reason to be isotropic, and the anisotropy appears due to the fact that α_x is always larger than α_y for both He and Ar atomic species and all T_g values for the rough surface. The coefficient α_z remains almost constant for Ar on both surface types but it increases with roughness for He. It must be noted that the c_z

Figure 4. Using the NP model, the values of the slip velocity $\hat{v}_k$, tangential stress $\hat{\sigma}_{kz}$, temperature jump $\Delta\hat{\theta}$, and normal heat flux $\hat{q}_z$ have been determined. All the values have been normalized by the method described in ref 10. The slopes of the lines provide the values of β coefficients. The $T_g = T_w = 300$ K gas velocities have been used to generate the NP kernel for He and Ar.

Table 3. Values of β Coefficients Determined by the Direct Employment of MD Velocities at 100, 200, and 300 K (eq 7), by the Use of MAC and EAC Parameters (eqs 6 and 11), and by the NP Model^a

surface	method	He			Ar		
		β_{1x}	β_{1y}	β_2	β_{1x}	β_{1y}	β_2
smooth	atomic	0.007	0.007	0.012	0.276	0.281	0.445
	M/EAC	0.006	0.006	0.009	0.272	0.269	0.425
	NP	0.008	0.008	0.012	0.303	0.299	0.431
rough	atomic	0.227	0.242	0.015	0.568	0.571	0.486
	M/EAC	0.206	0.185	0.013	0.528	0.520	0.462
	NP	0.215	0.191	0.016	0.555	0.546	0.503

^aThe values of β_{1x} , β_{1y} , and β_2 (MAC) are computed at $T_g = T_w = 300$ K.

collision clouds as shown in Figure 1 are more diffusive than the clouds of the other velocity components for both Ar and He. This behavior has also been found for CO₂ and CH₄ colliding on graphene.¹⁰ It can be seen as an indication that the normal component of the velocity is the main responsible component of the thermal exchange with the surface, i.e., of the displacements of the solid atoms due to the collision.

The gas temperatures after collision are dependent on the gas atom nature. The difference with respect to the target temperature before collision is much more marked for Ar than for He, in agreement with the most diffusive nature of the Ar collisions with gold. However, for both atom types, the gas atoms gain thermal energy when they are colder than the surface and lose a part of it after collision with a colder surface, in agreement with α_e variations. The coefficient α_e decreases with T_g for both atomic species and it is larger for Ar than for He, demonstrating once again that the He collisions are almost specular whereas the Ar collisions are almost diffusive. The roughness of the surface causes an increase of the α_e value for Ar, but it has almost no effect in the α_e value for He.

From Figure 1, it can be observed that although the reflective velocities are closer to the diffuse case on the rough surface, the value of the reflective energy still corresponds to the specular case. The results of Table 1 also show that the temperature change in the He flow is very small after the collision (below 6%). These evidences indicate that the diffusivity degree in velocity components is mainly due to the conversion of kinetic energy during the collision. As apparent from the pairwise potentials, the Ar atom interacts more strongly with the Au surface than the He atom. This conclusion can also be observed from the kinetic energy diffusivity in Figure 1 and the temperature change in Table 1.

The β coefficients obtained by the NP model are the slope coefficients, as presented in Figure 4. The NP kernel was originally developed for CH₄ and CO₂ on a graphite surface, for which the adsorption effect is more remarkable. For the He/Au–Au systems, the adsorption effect is weaker. Therefore, if we calculate the reflective energy using the reflective velocities produced by the NP model, its diffusivity degree will be overestimated. The alternative way is to directly generate the reflective energy, i.e., using $P(c^2/c'^2)$ to evaluate the term $\langle c'^2/2 - c^2/2 \rangle$ in eq 11 for the normal heat flux. We took the β value determined by the atomic wall as our benchmark and, by comparing the mean error of the NP model with the mean error of MAC (3.3 vs 11.9%), we found that the performance of the NP model is better. From the β values presented in Table 3, we can conclude that the roughness of the Au surface can significantly affect the friction coefficient of He and Ar noble gases at room temperature. However, the effect of surface roughness on thermal resistance is very limited.

Due to the reproduction of the roughness of the surface, our results can be compared with just a few data from the literature. Experimentally, it is as difficult to produce a perfectly smooth surface as to control its roughness. Karniadakis et al.²⁷ have reported a thermal momentum accommodation coefficient value of 0.073 for the He–Al pair. This value is consistent with the experimentally determined EAC value of 0.017 by Thomas and Schofield²⁸ at 320.15 K, confirming the very weak nature of interaction of He with metal surfaces and the quality of the present He–Au pairwise potential.

Hadj Nacer et al.¹ measured slip coefficients from He and Ar gas flows in a silicon microchannel covered with gold. They obtained β_1 values of 1.305 ± 0.018 and 1.342 ± 0.019 for He and Ar, respectively. These values are much higher than those presented in Table 3 for the rough surface, indicating that the present surface is not rough enough. In the experimental work of Hadj Nacer et al.,¹ the roughness of the gold coating, realized by vapor deposition, was evaluated at 0.87 nm. This value corresponds roughly to 6 times the gold atom bulk radius. The addition of only one more gold atom height on the smooth surface, as in the present rough surface, is certainly not sufficient to model this coating.

Trott et al.²⁹ have measured thermal accommodation coefficients from gas heat flux between plates at different temperatures. For the steel plates coated with gold and cleaned by plasma treatment, they obtained EAC = 0.85 for Ar and 0.31 for He, respectively at 296 K. These results are consistent with the α_e values presented in Table 1 if we consider once again that the experimental surface is rougher than the simulated one. It can also be noted that the final experimental roughness also depends on the steel surface quality before coating.

4. CONCLUSIONS

In summary, the extremely weak He–Au pairwise interaction potential has been derived from ab initio determinations for the first time. For this purpose, dispersionless density functional periodic calculations were combined with effective pairwise functional parameters for dispersion. These parameters were obtained from time-dependent DFT response theory using localized Hartree–Fock orbitals on He–Au_n clusters. The global interaction He–Au(111) potential reproduces accurately the best estimate of the well depth value (about 8 meV), whereas the standard vdW–DFT method greatly overestimates the attractive interaction. Next, the ab initio pairwise potential was used in molecular dynamics simulations of collisions of a He atom with a smooth Au(111) surface as well as a rough Au surface. The gas velocities recorded before and after the collision were employed to determine accommodation coefficients. These coefficients are the key ingredients to

model interface phenomena such as slippage or temperature jump, having further applications such as, for example, in macroscopic gas low simulations based on Navier–Stokes equations.

Different methodologies were applied and compared for the derivation of interface quantities: the use of atomistic velocities, of accommodation coefficients, and of an NP kernel constructed from a reduced number of simulations. The results obtained with the three methods compare very well, with the NP kernel approach having clearly a better performance than the treatment based on using accommodation coefficients. Our results allow to conclude that He gas flow has almost no friction effect on a smooth surface, but the friction is more pronounced on a rough surface. However, in both surface cases, the temperature transfer is almost nonexistent. The collisions of He on gold are then almost elastic.

For comparison purposes, molecular dynamics simulations using the same computational setup were carried out for Ar using the ab initio-based pairwise potential reported in our previous work.¹¹ As expected from the force field strength difference, the collisions of Ar with the gold surfaces are more diffusive than for He, and the friction effect and temperature jump are more pronounced for Ar flows on the rough gold surface. These results confirm the quality of the ab initio-based He–Au and Ar–Au pairwise potentials. It can also be concluded that improved simulations must consider surfaces with a much more pronounced roughness than that modeled in this work.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b03555.

Clusters and slabs used for the determination of the He–Au pairwise potential, electronic structure computational details, fitting analyses, and molecular dynamics computational details (PDF)

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Notes

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