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# Energy accommodation under non-equilibrium conditions for aluminuminert gas systems

Tejas Mane<sup>a</sup>, Pooja Bhat<sup>a</sup>, Vigor Yang<sup>b</sup>, Dilip Srinivas Sundaram<sup>a,\*</sup>

<sup>a</sup> Indian Institute of Technology Gandhinagar, Palaj, Gujarat, 382355, India

<sup>b</sup> School of Aerospace Engineering, Georgia Institute of Technology, Atlanta, GA 30332 USA

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#### ABSTRACT

Molecular dynamics (MD) simulations are conducted to determine non-equilibrium energy accommodation coefficients for aluminum-inert gas systems for a surface temperature of 300 K and gas temperatures in the range of 1000–3000 K. Three different gases are considered: helium, argon, and xenon. Density functional theory (DFT) simulations are conducted to obtain gas-surface interaction potentials and these are then fed as inputs to MD simulations. Effects of temperature and atomic weight of the gas on the accommodation coefficient are explored. Calculated accommodation coefficients are of the order of 0.1 and it is weakly dependent on gas temperature, in contrast to the predictions of Altman's model. Results suggest that energy accommodation coefficients are greatest for argon and lowest for helium for all temperatures considered in this study. This is explained by independently probing the effects of well depth and mass ratio and determining the relative importance of these two effects for the systems under consideration. Lorentz–Berthelot mixing rules substantially over predict the potential well depth, resulting in higher accommodation coefficients. The underlying physics and mechanisms are unraveled using a simple 1-D collision model.

### 1. Introduction

Aluminum (Al) particles are used in propulsion and energy-conversion applications due to their high energy density, relative safety, and low cost [1]. Micron sized Al particles, which are being currently employed, suffer from several drawbacks such as high ignition temperatures, particle agglomeration, and two-phase flow losses [2]. Al particles are covered by an aluminum oxide layer of thickness in the range of 2–4 nm [2]. Ignition of micron-sized Al particles occurs upon melting of the oxide layer at 2350 K [2]. The high ignition temperatures result in low energy release rates, thereby rendering Al micro particles unattractive for practical propulsion applications. Al nanoparticles have more favorable properties such as lower ignition temperatures and burning times due to their higher surface-to-volume ratios [2]. The ignition temperatures of Al nanoparticles are as low as ~933 K [2]. This has been attributed to the loss of integrity of the oxide layer due to Al core melting [3] and/or polymorphic phase transformations [4]. Substitution of Al nanoparticles for micron-sized counterparts thus offers substantial enhancements in the burning rates [5]. In order to develop next-generation energetic nanomaterials, understanding the ignition and combustion behavior of individual aluminum nanoparticles is necessary.

Prior experimental studies [6,7] on combustion of Al nanoparticles have shown that heat transfer between Al nanoparticles and ambient gas strongly influences combustion behavior. A shock tube was employed to measure combustion temperatures and burning times of Al nanoparticles in  $O_2/N_2$  and  $CO_2/N_2$  gases. In these studies, the particle size was in the range of 18–110 nm and the gas pressure varied in the range of 4–32 atm. Energy balance analysis was performed to predict burning times and combustion temperatures. As the particle size is comparable to the mean-free-path of gas molecules, a free-molecular regime model was used to determine heat-transfer rate,  $\dot{q}$  [8,9]:

$$\dot{q} = \frac{\alpha_E}{4} n_g v \left(\frac{1}{2} + \frac{C_v}{R}\right) k_B (T_p - T_g)$$
(1)

where  $\alpha_E$  is the energy accommodation coefficient (EAC),  $n_g$  the gas molecular concentration,  $\nu$  the average speed of gas molecules,  $C_{\nu}$  the molar constant-volume heat capacity of the gas, R the gas constant,  $k_B$  the Boltzmann constant, and T the temperature. The subscripts p and g refer to particle and gas, respectively. The energy accommodation coefficient is defined as the ratio of average energy transferred during collision to the theoretical maximum value under complete accommodation:

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<sup>\*</sup> Corresponding author. *E-mail address*: dilip.sundaram@iitgn.ac.in (D.S. Sundaram).

Table 1

Measured energy accommodation coefficients for Al-inert gas systems.

System		Energy accommodation coefficient ( $\alpha_E$ )		
	Al-He	0.073-0.074 [11], 0.53 [12], 0.38-0.47 [13]		
	Al-Ne	0.159–0.163 [11]		
	Al-Ar	0.334-0.343 [11], 0.81 [12], 0.91-0.96 [13], 0.75[14]		
	Al-Kr	0.488[11], 0.55[14]		
	Al-Xe	0.86 [12], 0.40 [14]		

[11] – Hot wire, T = 418-483 K,  $\Delta T = 35-180$  K; [12] – Parallel plate, T = 419 K,  $\Delta T = 23$  K; [13] – Parallel plate, T = 303 K,  $\Delta T = 10$  K; [14] – Concentric cylinders, oxidized Al, T = 500-800 K.

$$\alpha_E = \frac{\overline{E}_0 - \overline{E}_1}{\overline{E}_0 - E_S},\tag{2}$$

where  $\overline{E}_0$  and  $\overline{E}_1$  are the average energies of incident and scattered gas molecules respectively, and  $E_s$  the average energy of gas molecules in thermal equilibrium with the surface. It was shown that energy accommodation coefficients of the order of 0.005 are necessary to obtain good agreement between model predictions and experimental data [7].

It is apparent that quantitative knowledgebase of accommodation coefficient is necessary to accurately predict the ignition and combustion behaviors of Al nanoparticles. Previous experimental studies [10–16] have attempted to quantify accommodation coefficients for Algas systems, but these are limited to equilibrium or near-equilibrium conditions (as shown in Table 1). The measured accommodation coefficient is quite sensitive to experimental conditions such as surface roughness [16,14] and gas purity [17]. It is also a strong function of the molecular weight of the gas. Note that there are significant variations in the measured accommodation coefficients, possibly due to differences in experimental conditions.

Various theories have been proposed to elucidate the energy accommodation mechanism and predict the accommodation coefficients. One of the earliest theories, Baule's model [18], treats gas and surface molecules as hard spheres and applies energy conservation to obtain an expression for the accommodation coefficient. The model has been later improved by Goodman [19-21]. Note that the hard sphere collision theory is applicable for high incident energies. Another well-known theory is the classical lattice theory, in which the gas molecule interacts with the lattice and the energy exchange is calculated by solving the classical equations of motion [21]. Gas molecules of various incident energies are considered. However, the motion of the gas atom is typically restricted to one dimension and the gas atom directly interacts with only one surface atom. More specific models such as the cubes models [22,23] have also been proposed for lower incident energies. These models assume that the gas atom interacts with a single surface atom and the tangential velocities of the gas atoms remain conserved. Furthermore, an accurate gas-surface interaction potential and an estimate of the natural frequency of the surface atoms is required. Another notable work on non-equilibrium energy accommodation was conducted by Altman [8]. Average energy transfer between gas molecules and the surface is written in terms of the equilibrium distribution of energy of incident gas molecules. The principle of detailed balance was used to arrive at the following upper bound for the energy accommodation coefficient:

$$\alpha_E < \frac{1}{\left(2\frac{C_\nu}{R} + 1\right)} \frac{\Theta^2}{T_g T_s},\tag{3}$$

where  $\Theta$  is the Debye temperature. For temperatures representative of those in combustion chambers, Eq. (3) suggests that accommodation coefficients are 2–3 orders of magnitude lower than unity. The validity of this result needs to be established.

From the literature survey, it is apparent that existing theories and data on accommodation coefficients for aluminum correspond to limited sets of conditions. Most of the available experimental data is under equilibrium or near-equilibrium conditions. In practical combustion systems, highly non-equilibrium conditions prevail. During ignition, particle temperature is  $\sim 300$  K, whereas gas temperatures are as high as 3000 K. During combustion, particle temperatures can overshoot ambient gas temperatures by more than 1000 K. Furthermore, the pressure range of concern is 1–100 atm. Particle size and shape are two other important parameters; particle size is in the range of 0.01–100  $\mu$ m and the shapes of concern to propulsion applications include spherical nanoparticles and flake-like particulates [1]. It is necessary to determine accommodation coefficients for these different sets of conditions, so as to understand Al nanoparticle ignition and combustion [7].

High-fidelity simulation techniques such as molecular dynamics (MD) simulations can be used to accurately predict accommodation coefficients under non-equilibrium conditions [24,25]. Many of the assumptions of the classical theories and models can be relaxed to yield more accurate predictions. It can also provide insight on the underlying physics and allow us to study systems and conditions that are rather difficult to recreate experimentally. In the present study, MD simulations are conducted to calculate energy accommodation coefficients of Al/He, Al/Ar, and Al/Xe systems. An attempt is made to develop a broad quantitative database of accommodation coefficients for highly non-equilibrium conditions. Calculations are performed for a surface temperature of 300 K and gas temperatures in the range of 1000-3000 K, representing conditions during the heat-up and ignition stage. Density functional theory (DFT) simulations are performed to obtain accurate gas-solid interaction potential functions. These potential functions are then fed as inputs to the classical MD simulations for calculating the energy accommodation coefficients. To unravel the underlying physics and mechanisms, a simple 1-D collision model is employed. A systematic study is conducted to determine the effects of gas temperature, potential well depth, and gas molecular weight on the energy accommodation coefficient.

# 2. Theoretical framework

### 2.1. Molecular dynamics simulations

Classical MD simulations are conducted to calculate energy accommodation coefficients for nano-scale Al films in various inert gas environments. Fig. 1 shows the physical model of concern: energy exchange between nano-scale Al film and an inert gas atom. In the present study, helium, argon, and xenon gases are considered. The gas atom approaches the surface, interacts with the surface atoms, and then scatters. To get a statistically meaningful value of the accommodation coefficient, numerous collisions are simulated, corresponding to different gas atom velocities that are sampled from the Maxwell–Boltzmann velocity distribution. Each collision process is simulated and analyzed using MD simulations. All MD simulations are performed using the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [26].



Fig. 1. Physical model: energy exchange between an inert gas atom and nanoscale Al film.



Fig. 2. Initial configuration showing an inert gas atom placed over the nanoscale Al film.

Fig. 2 shows the initial configuration; an inert gas atom is placed over the nano-scale Al film at a distance of about 10 Å. An aluminum crystal (lattice spacing of 4.049 Å) with dimensions of 28 Å  $\times$  28 Å  $\times$  10 Å and containing 490 atoms is considered. Periodic boundary conditions are enforced along *x* and *y* directions. The film is surrounded by vacuum in the *z* direction. The aluminum crystal is equilibrated at 300 K and 0 bar pressure in an NPT ensemble for 50,000 time steps. The temperature and pressure are maintained using Nose-Hoover thermostat and barostat. The time step is chosen as 1 fs to resolve atomistic motion accurately. Time integration is performed using the velocity Verlet algorithm.

The velocities of inert gas atoms are sampled from the flux-corrected

Maxwell-Boltzmann (MB) distribution:

$$f(\mathbf{v}_{x,y}) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{mv_{x,y}^2}{2k_B T}\right),\tag{4}$$

$$f(v_z) = \left(\frac{m}{k_B T}\right) v_z \exp\left(-\frac{mv_z^2}{2k_B T}\right),\tag{5}$$

where *f* is the velocity distribution function, *m* the mass of the inert gas atom, *v* the velocity,  $k_B$  the Boltzmann constant, and *T* the temperature. Fig. 3 shows the velocity distribution for a helium gas at a temperature of 2000 K. A finite number of velocities are sampled from the distribution. Two sampling approaches are considered. In the first approach, the gas atom is positioned at the center (of the *x*-*y* plane) and 10,000 velocity sample points are employed. In the second approach, 500 velocity sample points are chosen randomly from the previous 10,000 dataset and 98 different gas atom positions in the *x*-*y* plane are considered. The second approach thus involves a total of 49,000 MD simulations to estimate the accommodation coefficient. As can be seen, the sampled velocities follow the flux corrected MB distribution reasonably well. A systematic study is also conducted to determine the sensitivity of predictions to changes in the number of sample points.

NVE-MD simulations are then conducted to simulate the collision and interaction of inert gas atoms with the nano-scale Al film. The accommodation coefficient is calculated as follows:

$$\alpha_E = \frac{m_g(\langle v_s^2 \rangle - \langle v_i^2 \rangle)/2}{2k_B(T_f - T_g)}$$
(6)

where  $\alpha_E$  is the energy accommodation coefficient,  $m_g$  the mass of the gas atom and  $\langle v^2 \rangle$  the average squared velocity. The subscripts *s*, *i*, *f*, and *g* refer to the scattered atom, incident atom, film, and gas, respectively.

The interactions between aluminum atoms are modeled using the embedded atom potential [27]. The optimized embedded atom



Fig. 3. Velocity distribution for a helium gas at a temperature of 2000 K; flux-corrected Maxwell-Boltzmann distribution.

#### Table 2

Gas-surface interaction potential parameters obtained using the classical Lorentz–Berthelot mixing rules.

Atom pair	$\varepsilon$ (meV)	σ (Å)
Al-Al [30]	392	2.62
He–He [31]	0.940	2.64
Ar–Ar [31]	10.33	3.405
Xe–Xe [32]	19.97	3.98
Al–He	19.196	2.63
Al – Ar	63.635	3.0125
Al – Xe	88.477	3.30

potential is obtained by fitting the potential to *ab initio* atomic forces of various atomic configurations such as surfaces, clusters, liquids and crystal at different temperatures [28]. To obtain accurate predictions, a proper gas-surface interaction potential is required. Typically, gas-surface interactions are modeled using the classical Lorentz–Berthelot (LB) mixing rules. Table 2 lists the potential parameters obtained using LB mixing rules. Although LB mixing rules are simple and convenient to model gas-surface interactions, it may substantially overestimate the potential well depth [29]. As a result, a more accurate treatment of gas-surface interactions is needed. It is well known that density functional theory (DFT) simulations can be used to obtain accurate interatomic potential functions.

# 2.2. Density functional theory (DFT) simulations

In the present study, accurate interatomic potential functions for Alinert gas systems are obtained using DFT simulations [33]. An FCC [001] aluminum crystal is employed and three different noble gases (argon, helium, and xenon) are considered. Simulations are performed to determine potential energies for different gas atom positions, in an effort to obtain adsorption energy curves. All DFT simulations are performed using Quantum Expresso (QE-5.4.0) package [34]. The adsorption energy is obtained by subtracting the ground state energies of isolated gas and Al systems from the combined system:

$$E_{Adsorption} = E_{Al+gas} - E_{Al} - E_{gas} \tag{7}$$

where *E* represents the energy.

Fig. 4 shows the simulation domain. A  $2 \times 2$  super cell of aluminum having 4 atomic layers is considered. Periodic boundary conditions are imposed in all directions. A vacuum spacing of 18 Å has been employed to minimize interactions between adjacent periodic images along the direction normal to the free surface. The supercell consists of 16 atoms of Al and 1 inert gas atom. A monkhorst-pack grid of size ( $8 \times 8 \times 1$ ) with a Gaussian smearing of 0.01 Rydberg, required energy cutoff, and a mixing ratio of 0.7 is employed. The top two layers are relaxed using the PBE/vdW-DF2 functional and the lattice constant is taken as 4.049 Å. The relaxation has negligible effect on the result. Parameter values are chosen such that convergence with respect to vacuum thickness, k-point mesh, and energy cutoffs are obtained. Table 3 shows the parameters used in the study. The cohesive energies of bulk aluminum ( $3 \times 3$  super cell) predicted by PBE and LDA pseudopotentials

Table 3	
Cutoff values (in Rydberg) used in DFT simulations.	

Pair-potential	Kinetic energy cutoff	Charge Density cutoff	
Al–He			
LDA	41	165	
vdW-DF2	45	215	
Al–Ar			
LDA	36	227	
vdW-DF2	36	225	
Al-Xe			
LDA	43	210	
vdW-DF2	43	210	

are 3.61 and 4.06 eV/atom, which are in reasonable agreement with values in the literature [35]. The phonon dispersion curves are obtained using Quantum Expresso package following the approach described in Ref. [36]. Comparison with experimental data [37] is also made. Results are provided in the supplementary materials section.

It is well known that van der Waals forces influence adsorption of an inert gas on Al surface. However, standard DFT approximations (such as LDA and GGA) do not consider nonlocal correlations (which are responsible for dispersion forces) or correlations outside the average screening length [38,39]. As a result, other non-local exchange-correlation functionals need to be considered. Several different functionals, including the local LDA/Perdew–Zunger [40], the semi local GGA/PBE, DFT D2/PBE [41], and non-local functionals namely such as vdW-DF1, vdW-DF2, OptB86b, and vdW-DF-cx are employed for the Al-Ar system. Based on the obtained results, a suitable functional is chosen and used for other inert gases. All vdW-DF calculations are performed using the PBE derived electron density [42–44].

Fig. 5 shows the adsorption energy curves obtained using DFT simulations. The following equation is used to curve-fit the DFT data and calculate the well depth and equilibrium spacing [45–47]:

$$V_{surf} = V_0 e^{-\gamma z} - \frac{C_3}{(Z - Z_0)^3},$$
(8)

where the  $V_0$ ,  $C_3$ ,  $Z_0$ , and  $\gamma$  are parameters determined by curve-fitting to the DFT data. Table 4 shows the calculated potential well depths and the equilibrium spacing for different gases. The adsorption energy increases with increasing atomic weight of the gas; it is greatest for xenon and lowest for helium. The PBE functional predicts less binding, whereas LDA and vdW-DF functionals predict much greater adsorption energies. Furthermore, the adsorption energy curves obtained using LDA and PBE exchange correlations decay at a much faster rate compared to non-local exchange correlations such as vdW-DF. This is not surprising, since LDA and PBE functionals do not account for long range interactions. For these reasons, vdW-DF2 has been adopted for all gases in the present study. To elucidate the charger transfer occurring during adsorption, charge density difference is computed in the following manner [48]:

$$\Delta \rho(r) = \rho_{Al/gas}(r) - \rho_{Al}(r) - \rho_{gas}(r), \qquad (9)$$

where  $\rho_{Al/gas}$ ,  $\rho_{Al}$ , and  $\rho_{gas}$  are the valence charge densities computed for



Fig. 4. Simulation domain consisting of an inert gas atom and 16 Al atoms used in DFT simulations.



Fig. 5. Adsorption energy curves for Al-inert gas systems obtained using DFT simulations.

Fable 4	
Potential well depth and equilibrium spacing for different inert gases obtained using DFT simulations.	

	LDA	PBE	DFT-D	vdW-DF1	vdW-DF2	opt-B86b	vdW-DF-cx
Al-Ar $D_e$ , meV $R_e$ , Å Al-He $D_e$ meV	-67.32 3.53 -15.53	- 16.21 4.19	- 69.63 3.79	-123.82 3.92	- 85.97 3.90	-82.81 3.84	-112.13 3.87
$R_{es}$ Å <b>Al-Xe</b> $D_{e}$ , meV $R_{es}$ Å	-114.39 3.79				-146.82 4.10		

the combined Al/gas system, Al, and gas, respectively. Results are shown in the supplementary materials section. Although similar trends are observed for all the three gases, the induced charge densities are greater for a heavier gas. This is not surprising as larger molecules have higher polarizability, resulting in greater adsorption energies. Furthermore, since vdW-DF2 functional uses the PBE derived charge densities, the induced charge densities are considerably lower than those obtained using the LDA exchange correlation. This result is consistent with the fact that the PBE exchange correlation predicts lower adsorption energies.

The adsorption energy curves can be used to obtain interatomic potential functions for gas-surface interactions. The gas-surface interaction energy of the combined system can be expressed as the sum of individual pair potential energies [49]:

$$V_{gs}(Z) = \sum_{i}^{Ncluster} U_{pair}(r_{ig}),$$
(10)

where Z is the distance of the gas atom above the surface. The

subscripts g and i refer to the gas atom and slab atom, respectively. In the present work, Morse potential is used to describe pairwise interactions

$$U_{pair} = D \left( e^{-2a(r_{ig}-R)} - 2e^{-a(r_{ig}-R)} \right), \tag{11}$$

where  $r_{ig}$  is the distance between the noble gas atom and metal atom taken into consideration.

Fig. 6 shows the comparison of interaction pair potentials obtained using LB mixing rules and DFT simulations for aluminum-inert gas systems. The potential well depth increases with increasing atomic weight of the gas; it is greatest for xenon and lowest for helium. As can be seen, LB mixing rules substantially over predict the well depth for all gases. DFT-derived potentials yield much better description of gas-surface interactions. For the determination of pair potentials, about 400 atoms are considered [49]. The potential parameters (*D*, *a*, and *R*) have been obtained by curve fitting the total interaction energy until a best fit determined by the optimization algorithm is achieved. Table 5 lists the parameters of the pair potential function for gas-surface interactions



Fig. 6. Gas-surface pair potentials for Al-inert gas systems: DFT simulations and LB mixing rules.

# Table 5 Parameters of the pair potential function for gas-surface interactions for aluminum-inert gas systems; vdW-DF2 potential.

System	D (meV)	<i>a</i> , Å <sup>-1</sup>	<i>R</i> (Å)
Al–He	1.44	1.26	4.47
Al–Ar	5.91	1.12	4.76
Al–Xe	7.93	1.00	5.12

for aluminum-inert gas systems. These potential functions are fed as inputs to the MD simulation routine for the calculation of energy accommodation coefficients.

## 2.3. 1-D collision model

Although MD simulations provide accurate predictions of accommodation coefficients for different conditions, it is often difficult to understand the underlying physics and mechanisms. In order to obtain deeper insights, a 1-D collision model, following the approach described in Refs. [21,50], is employed. Fig. 7 shows the schematic illustrating the 1D collision model. The solid atom (represented as a cube) is attached to its lattice position by a spring of known stiffness,  $k_{\rm spring}$ . The initial velocity of the gas atom follows the Maxwell–Boltzmann distribution. The interaction between the incident gas atom and solid atom is governed by the DFT-derived Morse potential (Eq. (11)). The governing equations of motion are given by:



Fig. 7. Schematic illustrating 1D collision model.

$$n_s \frac{d^2 x_s}{dt^2} = -k_{spring} x_s + F_{morse,s},\tag{12}$$

$$m_g \frac{d^2 x_g}{dt^2} = F_{morse,g},\tag{13}$$

where x denotes the position, m the mass, and  $F_{morse}$  the gas-solid interatomic force:

$$F_{morse} = -\frac{dU_{g-s}}{dx},$$
  
$$U_{g-s} = D\left(e^{-2a(x_{g-s}-R)} - 2e^{-a(x_{g-s}-R)}\right),$$
 (14)

where  $x_{g,s}$  is distance between gas and solid atoms. The subscripts *s* and *g* denote solid and gas, respectively. The parameters *a* and *R* are taken to be 1.26 Å<sup>-1</sup> and 4.47 Å, respectively. The stiffness of the spring is related to the oscillation frequency of solid atom:

$$f = \frac{1}{2\pi} \sqrt{\frac{k_{spring}}{m_s}}.$$
 (15)

The oscillation frequency is taken as  $4 \text{ ps}^{-1}$ , approximately equal to half the Debye frequency. The trajectories are computed using the leapfrog algorithm.

# 3. Results and discussion

# 3.1. MD simulation results

The MD simulation framework described in Section 2.1 is employed to calculate accommodation coefficients of aluminum-inert gas systems. As only a finite number of velocity sample points are considered, a systematic study is first conducted to study the sensitivity of predictions to the number of position and velocity sample points. Fig. 8 shows the calculated accommodation coefficients for different number of velocity sample points ( $n_v$ ) and number of positions ( $n_p$ ). The accommodation coefficient initially fluctuates, but then becomes nearly constant at around  $n_v = 500$ . Simulations become computationally intensive when more than 500 velocity sample points are used, while offering little improvement in accuracy. The accommodation coefficient is found to be relatively insensitive to changes in the number of positions, when 500 velocity sample points are used. As a result, using a single gas atom position and 500 different velocities appear to be sufficient to get reasonably accurate results.

Detailed analysis is performed to understand the dynamics of gassurface interactions. Fig. 9 shows the temporal evolution of position and kinetic energy associated with motion of gas atom along the z direction. The gas atom accelerates as it approaches the surface due to attractive forces exerted by solid atoms, thereby resulting in an increase in the kinetic energy. As it nears the surface, repulsive forces come into



Fig. 8. Sensitivity of model predictions to the changes in the number of position and velocity sample points; Al/Ar system,  $T_s = 300$  K.

play and the gas atom is deflected back.

Depending on the initial kinetic energy and energy exchange, the gas atom may overcome the attractive force field or continue to hop along the surface. In Fig. 9, two cases are shown corresponding low and high incident velocities along z-direction. For the high incident z-velocity case, the gas atom rebounds immediately, whereas hopping is quite evident for low incident z-velocities. In fact, a correlation between velocity of gas atom in the z direction and the number of hops was observed.

Fig. 10 shows accommodation coefficients for different gas temperatures obtained using two different sampling approaches. It is apparent that both sampling approaches give similar results. The gas temperature exerts a weak effect on the accommodation coefficient. This is in contrast to the strong temperature dependence predicted by Altman [8]. Furthermore, accommodation coefficients obtained in this study are of the order of 0.1, substantially greater than the predictions of Altman's model for similar temperatures. This suggests the possibility that the Altman's model underestimates accommodation coefficients at high temperatures. The accommodation coefficient is lowest for helium and highest for argon. Clearly, the accommodation coefficient is not a monotonic function of the gas atomic weight. The classical hard sphere model predicts that the accommodation coefficient increases with increasing mass ratio,  $\mu$ , and attains a maximum value at  $\mu = 1.0$ . The present study considers a relatively low surface temperature of 300 K and high gas temperatures (as high as 3000 K). The classical hard sphere model is thus relevant to this study. Note that the mass ratios of Al–He, Al–Ar, and Al–Xe systems are 0.15, 1.48, and 4.86, respectively. It is thus not surprising that the accommodation coefficient is lowest for helium. It is however important to recognize the fact that the applicability of the classical hard sphere model is restricted to  $\mu < 1$  [21]. For greater mass ratios ( $\mu > 1$ ), complexities such as hopping and multiple interactions need to be considered [21].

Heavier gases are associated with greater potential well depths and this may exert a secondary effect, which is not considered in the hard sphere model. To eliminate this complication and to isolate the effect of mass ratio on the gas-surface energy exchange, a numerical experiment is conducted. The atomic mass of the gas is varied, while keeping other



Fig. 9. Temporal evolution of position and kinetic energy associated with motion of gas atom along the z direction; aluminum-helium system at 3000 K.



**Fig. 10.** Accommodation coefficients of aluminum–inert gas systems for different gas temperatures obtained using vdW-DF2 potentials (open symbols  $\rightarrow$   $n_{v} = 500$ ,  $n_{p} = 98$ ; closed symbols  $\rightarrow$   $n_{v} = 10,000$ ,  $n_{p} = 1$ );  $T_{s} = 300$  K.

parameters such as gas temperature, substrate temperature, and potential function constant. Fig. 11 shows the result of this numerical experiment. The energy accommodation coefficient increases with increasing mass ratio, attains a maximum value at  $\mu \sim 0.6$ , and then decreases with further increase in the mass ratio. This has little to do with hopping and more to do with effectiveness of gas-solid energy exchange, since a vast majority of the atoms does not hop and the hopping scenario is nearly the same for all mass ratios. Note that the obtained trend is consistent with the results of a more accurate hard sphere analysis, which predicts that the accommodation coefficient for a 3D lattice decreases with increasing mass ratio for  $\mu > 1$  and increases with increasing mass ratio when  $0 < \mu < 0.84$  [51]. The former trend may be attributed to the fact that the energy transfer is less efficient for slowly varying forces [21]. Slowly varying forces are observed for heavier gases, since the average speed of gas atoms is lower for a heavier gas at the same temperature. The trend shown in Fig. 11 also appears to explain qualitatively the effect of gas atomic weight on the accommodation coefficient.

To elucidate the effect of potential well depth, another numerical experiment is conducted in which all parameters are held constant, except the potential well depth. Al-He system is chosen and the gas and surface temperatures are taken to be 3000 K and 300 K, respectively. Fig. 12 shows the effect of potential well depth on the accommodation coefficient for Al-He system. It is apparent that accommodation coefficient increases with increasing potential well depth. Potentials obtained using DFT simulations and LB mixing rules offer similar predictions for the same well depth. The study also provides clear evidence



Fig. 12. Effect of potential well depth on the accommodation coefficient for aluminum – helium system;  $T_g = 3000$  K and  $T_s = 300$  K.



Fig. 13. Hop count for potentials obtained using the LB mixing rule and DFT simulations for aluminum-helium system;  $T_g = 3000$  K and  $T_s = 300$  K.

that the LB mixing rule significantly over predicts accommodation coefficients of metal-gas systems. To understand the effect of well depth, the number of hops is counted for both cases and compared. This is shown in Fig. 13. Increasing the well depth facilitates more hopping. Intuitively, hopping results in more residence time and could favor thermal equilibration of gas molecules with the surface. It is thus not surprising that LB mixing rules overestimate accommodation



Fig. 11. Effect of mass ratio,  $\mu$ , on (a) accommodation coefficient, (b) hop count; other parameters such as gas and substrate temperatures and potential function are held constant.



Fig. 14. Number of hops for gas temperatures of 1000 K and 3000 K;  $T_s = 300$  K.

coefficients.

In the two numerical experiments, effects of potential well depth and mass ratio were explored independently by holding other parameters and conditions constant. In reality, changing the atomic mass alters both the well depth and mass ratio and these effects operate simultaneously. Furthermore, temperature dependence of accommodation coefficient and hopping phenomenon needs to be explored for systems and conditions under consideration. For these reasons, the number of hops is calculated for different gases and different gas temperatures. Results are shown in Fig. 14. For both temperatures, the number of hops is greatest for xenon and lowest for helium, suggesting a clear connection between gas atomic weight and number of hops. This is not surprising, since heavier gases are associated with deeper potential wells and lower velocities at the same temperature. Although the well depth is greatest for xenon, mass ratio  $(\mu)$  appears to exert a stronger effect on the overall energy exchange, resulting in lower accommodation coefficients for xenon when compared to argon. With increasing temperature, the distribution shifts slightly towards the left, but the hopping scenario is not drastically different, which perhaps explains the weak temperature dependence of the accommodation coefficient. The observed temperature dependence is also in agreement with the classical hard sphere model predictions, which suggest that the accommodation coefficient is independent of the gas temperature.

### 3.2. 1-D collision model predictions

The collision model is employed to determine the effects of gas atom mass, temperature, and well depth on the accommodation coefficient. An attempt is made to unravel mechanisms by which these parameters affect the energy exchange process and explain MD simulation results.

## 3.2.1. The mass effect

Accommodation coefficients are calculated for different gas atom masses and the effect of mass ratio is first explored. Fig. 15 shows the effect of mass ratio on the accommodation coefficient. As can be seen, calculations are conducted for different well depths, but the effect of well depth will be discussed in a separate section. The accommodation coefficient increases with increasing mass ratio, attains a maxima, and then decreases with further increase in the mass ratio. The obtained trend is qualitatively consistent with MD simulation results. For mass ratios lower than  $\sim 0.3$ , gas velocities are quite high and the effect of lattice forces is expected to be insignificant. As the momentum of the gas atom increases with increasing gas atom mass, the solid atom gains more momentum for the case of a heavier gas atom. As a result, the accommodation coefficient increases with increasing mass ratio, as predicted by the classical hard sphere collision theory. For mass ratios greater than  $\sim 0.3$ , an opposite trend is observed. In order to understand the underlying mechanism, the temporal evolution of position,



**Fig. 15.** Effect of mass ratio on the accommodation coefficient;  $T_s = 0$  K,  $T_g = 2100$  K; 1-D collision model predictions.

kinetic energy, impulse, and force are calculated and these are shown in Fig. 16. As the gas atom mass increases, its velocity decreases, resulting in greater interaction times. As a result, the effect of lattice forces may no longer be negligible. Fig. 17 is a schematic showing the evolution of positions of gas and solid atoms. As the gas atom approaches the solid, the solid atom moves upward due to attractive forces and is then pushed backward due to repulsive forces. For  $M_g = 10$  amu, the motion of gas and solid atoms are largely out of phase with each other during the rebound stage. For a heavier gas atom ( $M_g = 30$  amu), on the other hand, the solid atom spring backs when the gas atom rebounds, resulting in an in-phase motion. Intuitively, for an in-phase motion during the rebound stage, interaction times are greater and the repulsive forces work against the solid atom motion. This diminishes the overall energy exchange and accommodation coefficient. The proposed mechanism [21] explains the reduction in accommodation coefficient with increasing mass ratio (shown in Figs. 11 and 15). An animation/video of the interaction process is included in the supplementary materials section.

# 3.2.2. The gas temperature effect

Fig. 18 shows the effect of gas temperature on the accommodation coefficient. As can be seen, the accommodation coefficient increases with increasing gas temperature, more so for  $\mu = 0.3$ . The temperature dependence of accommodation coefficient is a function of gas molecular weight. This is in qualitative agreement with MD simulation results (see Fig. 10). To understand this trend, snapshots of gas and solid atom positions are analyzed. These are shown in Fig. 19. For a mass



**Fig. 16.** Temporal evolution of (a) position, (b) kinetic energy, (c) impulse, (d) force for 3 different gas atom masses (10, 20, and 30 amu) and for a fixed solid atom mass of 27 amu. Solid lines correspond to the gas atom and dashed lines correspond to the solid atom;  $T_s = 0$  K,  $T_g = 2100$  K, D = 8 meV; 1-D collision model predictions.



Fig. 17. Snapshots of gas and solid atom positions for gas atom masses of 10 and 30 amu and for a solid atom mass of 27 amu.  $T_s = 0$  K,  $T_g = 2100$  K, D = 8 meV.



**Fig. 18.** Effect of gas temperature on the accommodation coefficient for a solid atom mass of 27 amu;  $T_s = 0$  K, D = 8 meV; 1-D collision model predictions.

ratio of 0.05, increasing the temperature from 1400 K to 2800 K does not substantially affect the energy exchange process. The gas and solid atom motions remain largely out of phase with each other. Similarly, for a mass ratio of 1.2, the gas and solid atom motions are in phase with each other, regardless of the temperature. The accommodation coefficient is thus a weak function of the gas temperature. On the other hand, for an intermediate mass ratio of 0.3, there is a clear shift from the inphase mode to the out-of-phase mode when temperature increases from 1400 K to 2800 K, resulting in an increase in the accommodation coefficient. An animation/video of the interaction process is included in the supplementary materials section.



Fig. 19. Snapshots showing gas and solid atom positions for three different mass ratios of (a)  $\mu = 0.05$ ; (b)  $\mu = 0.3$ ; (c)  $\mu = 1.2$ ;  $T_s = 0$  K, D = 8 meV; 1-D collision model predictions.

# 3.2.3. The well depth effect

Accommodation coefficients are calculated for different well depths in an attempt to elucidate the effect of well depth. Fig. 20 shows the effect of well depth on accommodation coefficient for different mass ratios. It is apparent that the accommodation coefficient increases with increasing the well depth, consistent with MD simulation results. As before, the temporal evolution of position, kinetic energy, impulse, and force are calculated (see Fig. 21). Clearly, increasing the well depth increases interatomic forces and reduces interaction times. As mentioned before, energy exchange becomes more efficient for shorter interaction times. For these reasons, an enhancement in accommodation coefficient is observed. This perhaps is also responsible for the prolonged hopping of the gas atom along the surface (shown in Fig. 13). An animation/video of the interaction process is included in the supplementary materials section.

# 4. Conclusions

Molecular dynamics simulations are conducted to calculate nonequilibrium energy accommodation coefficients for aluminum-inert gas systems for a surface temperature of 300 K and gas temperatures in the range of 1000–3000 K. Three different gases are considered: helium, argon, and xenon. DFT simulations are conducted to determine accurate gas-surface interaction potentials and these have been compared with the potentials obtained using the classical Lorentz–Berthelot mixing rules. Effects of gas temperature and molecular weight on the accommodation coefficient are determined. A 1-D collision model is used to understand the MD simulation results. The major conclusions of the



**Fig. 20.** Effect of well depth on the accommodation coefficient for different mass ratios;  $T_s = 0$  K,  $T_g = 2100$  K; 1-D collision model predictions.

present study are:

- Lorentz–Berthelot mixing rules substantially over predict the potential well depths for Al-inert gas systems. This results in more energy exchange and hopping of the gas atom along the surface, thereby resulting in higher accommodation coefficients. DFT derived potentials predict smaller well depths and lower accommodation coefficients.
- 2. The calculated accommodation coefficients are of the order of 0.1, substantially greater than the predictions of Altman's model for similar temperatures. This suggests that Altman's model

underestimates accommodation coefficient at high temperatures.

- 3. When other parameters and conditions are held constant, the energy accommodation coefficient increases with increasing mass ratio, attains a maximum value at  $\mu \sim 0.6$ , and then decreases with further increase in the mass ratio. This trend has little to do with hopping and more to do with effectiveness of gas-surface energy exchange. The initial rise can be explained by the classical hard sphere collision theory, whereas the latter trend is attributed to the effect of lattice forces. The gas and solid atom motions become inphase with each other during the rebound stage as the mass ratio increases beyond a threshold value, diminishing the energy exchange.
- 4. Increasing the potential well depth leads to more hopping of the gas atom along the surface and greater accommodation coefficient. As the well depth increases, interatomic forces increase and interaction times decrease, resulting in more energy exchange and greater accommodation coefficients.
- 5. The present analysis also predicts a weaker gas temperature dependence of the accommodation coefficient than the Altman's model. The gas temperature effect is stronger for argon when compared with helium and xenon. Increasing the gas temperature increases the gas atom velocity and decreases the interaction times. The gas and solid atom motions become out-of-phase with each other during the rebound stage, resulting in a greater accommodation coefficient. This effect is stronger for intermediate mass ratios (e.g., Al/Ar system), for which a shift from the in-phase mode to the out-of-phase mode is possible.
- 6. Energy accommodation coefficients are greatest for argon and lowest for helium. Increasing the atomic weight of the gas increases the potential well depth and mass ratio. However, the mass ratio is found to exert a more dominant effect, thereby resulting in higher



**Fig. 21.** Temporal evolution of (a) position, (b) kinetic energy, (c) impulse, (d) force for 3 different well depths of 1, 8, and 25 meV. Solid lines correspond to the gas atom and dashed lines correspond to the solid atom;  $T_s = 0$  K,  $T_g = 2100$  K,  $\mu = 0.37$ ; 1-D collision model predictions.

accommodation coefficients for argon when compared to helium and xenon.

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#### Supplementary materials

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