Thermal accommodation at cold Ar atoms collisions with small Fe clusters at different temperatures

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Abstract. Thermal accommodation coefficients at collisions of solitary argon atoms at room temperature with iron clusters at temperatures 200–2500 K are calculated. Molecular dynamics method is applied. Finnis–Sinclair potential is used to describe interaction between iron atoms in clusters. The incident atom interacts with a cluster through the Buckingham potential. The number of incident atom trajectories is from 10000 to 100000. Initial velocities of incident atoms obey the Maxwell distribution. Thermal accommodation coefficient is calculated for 2 sizes of cluster, 9 and 27 atoms.

1. Introduction

Nanoparticles find currently wider and wider usage in industry. One of them is catalysts [1], because of the large ratio of their surface area to the unit volume. Nanoparticles can also be used for improving the performance of photovoltaic materials. Several other applications are ameliorating dyes and oils [2–4] and black carbon [5]. Simulation of parameters of submicron particles formed in combustion products of coals is treated in [6].

Time-resolved laser-induced incandescence is a way to obtain nanoparticle size distribution. However, one needs thermal accommodation coefficient to interpret the data. The values of the coefficient are calculated by the molecular dynamics (MD) method [1].

Besides practical applications, there are unsolved theoretical problems [7]. The differences of experimental data and the classical nucleation theory can exceed several orders of magnitude. There is also an opposite problem. Theoretical studies can not be proved by experiment because of the insufficient level of the measurement technique. Relatively high temperature conditions create the obstacle. Heat transfer between soot particles and surrounding gas is studied both theoretically and experimentally [8].

Multiscale approach [9] is developed in 1991 to treat condensation kinetics in supercooled vapors. Condensation of iron behind the shock wave is studied using MD. Clusters of up to 13 particles are simulated and their interaction with incident atoms is investigated. The Lennard-Jones potential is used. Nucleation rate is calculated. It is confirmed that FeCO molecules participate in the condensation process.

Another approach to the nucleation process is considered in [2–4, 10]. The probabilities of attachment and evaporation, which are crucial to determining the rate constants in the kinetic approach, are calculated by classical nucleation theory. Condensation is statistically investigated: number and size of clusters are measured at each time moment. A system of
Figure 1. Characteristic examples of two incident Ar atom trajectories for \( N = 9 \) and cluster atom temperatures 500 K (a, b, c) and 2500 K (d, e, f): trajectory projections on \( xz \) (a, d) and \( yz \) (b, e) planes and velocity profiles (c, f). \( r \) is an impact parameter, \( v_i \) is an initial velocity.

10 000 atoms of copper and argon is studied. The Cu atoms interact with each other through the embedded atom method potential. The interactions between Ar atoms and between Ar and Cu atoms are described by the Lennard-Jones potential. The dependence on the number of atoms in the cluster of the potential barrier between the vapor atoms and the cluster is calculated in [2]. The temperature range from 300 to 2000 K is studied. In [3], a histogram of size distribution of nanoparticles deposited on the walls is calculated. Various conditions of modelling are tested in [4]. In addition, probabilities of dimerization and effectiveness of small clusters cooling is studied in [10]. A method of direct numerical solution for simulation of bulk condensation of supersaturated vapor is used in [11].

This work is aimed at calculating thermal accommodation coefficients for a number of temperatures and several sizes of clusters. MD method is used. The MD details are described in section 2. Section 3 is devoted to the calculation of the accommodation coefficient. The definition, the method of calculation and the results obtained are presented.

2. Model and method
The cluster is created in a manner similar to that described in [1]. First, the iron atoms are placed in sites of the \( bcc \) lattice in the spherical region that belongs to the space under consideration. Lattice parameter \( \sigma = 2.866 \) Å. Finnis–Sinclair potential is used for describing interactions between these atoms. The interaction between Ar and Fe atoms is taken in the form of the Buckingham potential [12]:

\[
U(r) = Ae^{-r/B} - C/r^6,
\]

where \( A = 4617 \) eV, \( B = 0.2752 \) Å, \( C = 70 \) eV Å\(^6\), cutoff radius is \( 2.5 \sigma = 7.165 \) Å.

The initial velocities of cluster atoms obey the Maxwell distribution at an arbitrary cluster temperature. Then, the cluster is heated using Langevin thermostat to the desired temperature.
At this point, the pressure inside the cluster is determined. This pressure is above the triple and below the critical point of the bulk matter.

Two examples of the incident atom trajectories are presented in figure 1 together with cluster atoms. The radius of atom is chosen from design reasons, the positions of atoms’ centres-of-mass are averaged over MD runs. For each MD run, the value of velocity $v_i$ is chosen in a random way according to the Maxwell distribution for 300 K. Atom coordinates and their dependencies on time agree with each other in figure 1, in (d-f) in particular. We see also the change of trajectory character with the increase of temperature.

Simulation of the trajectory continues until the atom leaves the zone where it may interact with the cluster (figure 1a,b,d,e). The timer of interaction starts, when the atom is at a distance, which is greater than the cutoff radius by 0.5 Å. It stops, when atom reaches this distance again. It defines the interaction time.

The impact parameter $r$ belongs to a uniform grid. Its minimal value is 0 and maximal value equals to the sum of the cluster radius and the cutoff distance of the potential. The step is chosen to obtain about 20 points of the partial accommodation coefficient. This number permits to achieve a balance between the errors for each point and for the average value of the accommodation coefficient at given temperature and number of atoms in the cluster.

3. Thermal accommodation coefficient

Thermal accommodation coefficient is a measure of energy transfer between the incident atom and the cluster. It is equal to the ratio of the decrease of energy of the atom to the temperature difference between the incident atom Maxwellian distribution and the cluster [1]:

$$\alpha = m(v_f^2 - v_i^2)/[4k_B(T - T_g)],$$  

where $m$ is a mass of the incident atom, $v_f$ and $v_i$ are velocities of the incident atom after and before the collision with the cluster, $k_B$ is Boltzmann constant, $T_g$ and $T$ are incident atom velocity distribution and cluster temperatures. The values of $\alpha$ are positive both for $T > T_g$ and $T < T_g$ since the nominator is also positive and negative in these cases.

The results obtained for each trajectory are averaged over a number of trajectories with the same value of the impact parameter. The obtained dependence has an approximate plateau till some value of the impact parameter then it drops to zero near the distance of the interatomic interaction potential cutoff (figure 2a). The second averaging is performed for a part of the graph where the coefficient is supposed to be constant. This value is shown as a red line.

Total number of MD runs is equal 100000 for $N = 27$ and temperatures above 500 K, and is 10000 in other cases. $N$ is the number of atoms in a cluster.

The calculations are performed for 8 temperatures from 200 to 2500 K. Clusters of 9 and 27 atoms are considered. The dependence of energy transfer on temperature is presented in figure 2b. It crosses zero value when temperatures of clusters and Ar atoms are equal to each other. Figure 2b shows that the energy exchange between the atom and the cluster grows when the cluster temperature increases.

However, the thermal accommodation coefficient decreases while the temperature rises (figure 3a). This falling dependence is explained by the faster increase of the denominator. It can be related to the decrease of interaction time with increase of temperature (figure 3b). The efficiency of the energy exchange decreases with the decrease of interaction time.

Diverse cluster properties are size-dependent as $N^{-1/3}$, when $N^{-1/3}$ tends to zero, since the dependence is defined by the ratio of the surface energy, which is proportional to $N^{2/3}$, to the volume one, which is proportional to $N$ [13, 14]. The results presented in figure 4a do not contradict such an $N$-dependence.

The increase of $\alpha$ with $N$ is related to the growth of the interaction time of an incident atom with a cluster with increase of $N$ (figure 4b).
Figure 2. Dependence of the energy transfer \( m(v_f^2 - v_i^2)/(4k_B) \) on the impact parameter for \( N = 27 \), \( T = 2500 \) K, where the arrow indicates the value of \( R \) and the red line is the average value of the coefficient (a), and temperature for 2 numbers of atoms in the cluster (b).

Figure 3. Dependencies on temperature of thermal accommodation coefficient (a) and interaction time for \( N = 9 \) (b).

The interaction time increases significantly with the decrease of cluster temperature. The colder cluster is the longer it takes for an argon atom to increase its energy enough to leave the cluster. The Finnis–Sinclair potential describes melting and it is not appropriate for higher temperatures [1]. As a result, the upper scope of applicability of the described accommodation coefficient calculation method is the boiling temperature of iron.

Accommodation coefficients are measured experimentally for large clusters in [15–17]. The obtained values are about 0.1. Further calculations are necessary for different Ar-Fe interaction potentials and larger clusters to perform reliable comparison of MD modelling and simulation to the experimental results and previous calculations [1].
4. Conclusion

The molecular dynamics method is applied to the calculation of the thermal accommodation coefficient for argon atoms at room temperature colliding with Fe clusters at temperatures in the range $T = 200–2500$ K. The following results are obtained:

(i) The dependence on impact parameter has a plateau corresponding to the actual value of the thermal accommodation coefficient.

(ii) Thermal accommodation coefficient decreases while the temperature rises.

(iii) Thermal accommodation coefficient increases with the growth of the particle number $N$. Linear dependence on the inverse cube-root of $N$ is expected for $N$ greater than $10^2$.

(iv) $N$ and $T$ dependencies of the duration of the interaction of incident Ar atom with the cluster are obtained.

(v) The dependencies calculated in items 2, 3 and 4 turn out to be consistent with each other.

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