Sticking coefficient for Fe atoms interacting with iron cluster

D Yu Lenev and G E Norman

1 Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13
Bldg 2, Moscow 125412, Russia
2 National Research University Higher School of Economics, Myasnitskaya 20, Moscow 101000, Russia
E-mail: lenevdy@mail.ru

Abstract. Fe atoms sticking to iron clusters is studied using molecular dynamics method. The interaction between the single atom and the solitary cluster is considered. A number of trajectories with different starting conditions is obtained. Dependencies on cluster and incident atom temperatures are studied. The coefficient decreases if any of these temperatures grows. The dependence on cluster size is also obtained.

1. Introduction
Metal nanoparticles are utile industrial objects. Their main application is catalysts, because of their high ratio of effective surface to volume [1]. Dyes, oils and protective covers can also benefit from metal nanoparticles [2–4]. However, their size distribution should be known to use them. Sticking coefficients (α) are needed to define this function. The α values can be calculated by molecular dynamics (MD).

Kinetics of condensation is studied in several works. Fe condensation behind the shock front is investigated by MD in [5]. The interaction between clusters and incident atoms is studied for clusters of less then 14 particles. The aims are to obtain the condensation rate and to confirm FeCO molecules participation in the process by using the values of the sticking, excitation and stabilization coefficients. Daun et al [1] also apply MD to model the condensation process. It is used to estimate the values of thermal accommodation coefficient. This coefficient describes the effectiveness of energy exchange between the incident atom and the cluster. Then, it is used to interpret the data of the time-resolved laser-induced incandescence (Ti–Re LII) and to obtain the cluster size distribution.

The growth of metal nanoparticles is also studied by MD in [2–4, 6]. 10 000 copper atoms in noble bath gases are considered. The sticking and vaporization coefficients are defined using classical nucleation theory. However, the author mentions, that they should be calculated by methods similar to one described below. The condensation process is described statistically. Number of clusters and their sizes are calculated during the whole simulation. The interaction between copper atoms occurs through the embedded atom method (EAM) potential. Cu–Ar and Ar–Ar interactions are described using Lennard-Jones potential. Potential well depth between the cluster and surrounding gas is calculated in [2]. The temperatures considered are from 300 to 2000 K. Cluster energy distribution is studied in [3]. Both translational and rotational energies
are taken into consideration. Size distribution of the particles condensed on the walls is presented in [4]. A wide range of simulation parameters is varied in [6], for example, temperatures of the bath gas, proportions of metal atoms and bath gas and methods of keeping the pressure constant.

There are other methods of modelling nucleation. The processes of nucleation, growth and decay of clusters are described by using cluster size distribution in [7]. The system of equations is written for this function and it is solved for several cases.

There are quite a lot of experimental works on the topic. [8] describes the process of nanoparticle formation as a result of supersaturated gas condensation. All stages of the process are covered: nucleation, growth and coagulation. Three methods of nanoparticle sizing are applied simultaneously: Ti–Re LII, laser light absorption measurement and electron emission method. One of the goals of [8] is obtaining sticking coefficients by theoretical processing of experimental data. The reverse process is considered in [9]. It is vaporization of iron and carbon nanoparticles, induced by laser light. The aim of the work is a simultaneous application of Ti–Re LII and laser light absorption measurement to analyze the dependence of the process on the size and nanoparticle formation conditions. Condensation of supersaturated vapour is studied in [10, 11]. The objects are water and soot. Paper [10] is devoted to the significant difference between experimental data and classical theory of nucleation. Condensation in laminar and diffusion chambers is investigated. The growth of nanoparticles is studied in [11] at pyrolysis of ethylene and argon mixture.

The goal of the present work is calculation of sticking coefficient for a number of cluster (T) and incident atom (Ta) temperatures and several sizes of cluster.

2. Model

Primarily, a cluster is created at several steps. First, spherical region is chosen. Then, atoms are placed in sites of the lattice, which happened to be inside the region. Since iron cluster is investigated, the lattice is body-centered and its period is 2.866 Å. Atoms of the cluster have velocities, which correspond to the Maxwell distribution for 300 K initially. The desired temperature is achieved at equilibration by using the Langevin thermostat. Fe atoms of the cluster interact through the Finnis–Sinclair potential of the EAM type.

The Lennard-Jones potential is used for the interaction between incident atoms and the cluster

\[ U(r) = \begin{cases} 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6], & r < r_{\text{cut}}, \\ 0, & r > r_{\text{cut}}, \end{cases} \] (1)

where \( U \) is potential energy, \( r \) is interatomic distance, \( \varepsilon = 1.05 \times 10^{-12} \) erg, \( \sigma = 2.95 \) Å [5], \( r_{\text{cut}} = 5 \sigma = 14.75 \) Å. Coordinates and initial velocities of incident atoms are needed to be defined. Initial coordinates belong to one plane and are at the same distance from the center-of-mass of the cluster. The impact parameter is changed with a permanent step and it has 25 different values between zero and approximately the value, where the sticking coefficient drops significantly.

The velocity of the incident atom is different for every trajectory and is chosen randomly using the Maxwell distribution for the specified temperature. This temperature is referred to as the temperature of the incident atom.

3. Calculation and results

Sticking coefficient \( \alpha \) is a ratio of the number of trajectories of atoms, which stick to the cluster, to the total number of trajectories. The fact of sticking is defined using by both time and energy criteria. Firstly, the atom should stay in the zone, where it interacts with the cluster, more than 30 ps. This time is one order of magnitude more than it takes the atom to hit the cluster and move away immediately. The time of interaction can be obtained from velocity profiles of
Figure 1. The dependence of sticking coefficient on impact parameter for cluster of 27 atoms, $T = 1500$ K, $T_a = 300$ K (a) and on $T$ for clusters of 9 and 27 particles and $T_a = 300$ K (b). The horizontal line corresponds to the average value of the sticking coefficient on the plateau. The arrow shows the distance between the cluster center-of-mass and the farthest cluster atom.

trajectories. The second criterion means that the total atom energy, which is the sum of the kinetic and potential energies, goes below zero. Initial energy of the incident atom is positive because there is no interaction with cluster atoms. This energy can be lost during collision with cluster atoms. If it remains positive, the atom can leave the cluster.

The dependence of sticking coefficient on impact parameter is shown in figure 1(a). There are two intervals of this dependence: a plateau and a decrease. The values of $\alpha$ are obtained by averaging of the points which belong to plateau for the current temperatures and cluster size. The decrease starts right after the plateau ends and continues until the value is almost zero. The border is defined visually. The existence of the $\alpha$ decrease can be explained by the rise of the distance between the cluster and the incident atom.

One can see the decrease of the sticking coefficient with increase of temperature in figure 1(b). The most possible reason is that the incident atom has greater chances to get enough energy to leave the cluster, if the cluster temperature is high. The calculations are conducted for clusters of 9 and 27 atoms. Coefficient for 9 atom cluster appeared to be smaller. The energy of a greater cluster is lower, so it is easier to stick to it.

Calculations are made for a cluster of 27 atoms for different incident atom temperatures, figure 2(a). The greater is the energy of the incident atom, the more of it the atom should lose to be able to stick to the cluster. So, sticking coefficient falls while the temperature rises.

The dependence on $N^{-1/3}$ is shown in figure 2(b). It is close to linear, 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 $N$. Measurements of the sticking coefficient in vacuum are not known to the authors. The values of sticking coefficient are calculated in [8] using the experimental data. They depend on the bath gas, used in experiment. All bath gases are at room temperature. The reason is different speed of cooling of the nanoparticles and Fe atoms, though all bath gases are at room temperature. The results of this work, where there is no bath gas and collisions are happening in vacuum, are close to [8], when Xe is the bath gas. The value of the coefficient in this case is approximately 0.1. So, the results are the same if one supposes that the clusters and incident atoms are cooled to the room temperature.
4. Conclusions
Molecular dynamics method is used to obtain the values of sticking coefficient for incident iron atoms colliding with clusters of 9 and 27 particles in vacuum at different cluster and incident atom temperatures.

Dependence of the sticking coefficient on the impact parameter has a plateau which gives the actual value of sticking coefficient.

Sticking coefficient drops while either temperature of the cluster or the temperature of the incident atom velocity distribution rises.

Sticking coefficient grows as $N^{-1/3}$ while cluster size increases.

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