Mass transfer in platinum by crowdion clusters initiated by the impact of a Pt$_2$ molecule

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Abstract. This work presents a molecular dynamics study of the propagation scenario of the crowdion complex initiated in the platinum crystal by means of atom or molecule bombardment with parallel and non-parallel orientations. The obtained results enable to conclude that the crowdion initiated by the Pt$_2$ molecule bombardment is significantly more effective for the mass transfer comparing to the crowdion excited by the single atom impact. It was detected that the atoms involved in the crowdion motion bear a vibrational mode with the frequency above the phonon spectrum. The obtained results contribute to the understanding of the mechanisms of mass transfer under equilibrium conditions.

1. Introduction
Crowdions - interstitial atoms located in closely-packed atomic rows, play an important role in relaxation processes in metals and alloys under severe external impacts, effectively transferring mass and energy. It is necessary to study the dynamics of crowdions in pure metals, as well as to analyze and compare the results obtained for various metals. The authors recently show that the concept of a supersonic crowdion can be extended to N-crowdion, where not one, but N atoms move at a high speed along a close-packed row. Experimental study of interstitial atoms moving along a crystal lattice at supersonic speeds encounters serious technical difficulties, that, in turn, promotes the study of these small scale phenomena by means of numerical methods including ab-initio simulations [1] and molecular dynamics. The latter has earlier been proved to be a powerful tool for investigation of small scale phenomena like phase transformations [2–5], mass and energy transfer [6–9], evolution of mechanical characteristics of the material subjected to various external impacts [10–15], analysis of nonlinear dynamics of the lattice [16–21], and many other structure evolution features. This work deals with the simulation of the one-dimensional (1D) propagation of 1- and 2-crowdions in fcc Pt lattice.

2. Simulation details
The simulation is performed for computational cells in the form of a parallelepiped having dimensions of 138×38×40 nm (Figs. 1). The cells consist of 14,400 atoms of Pt that form the fcc structure. Periodic boundary conditions are applied along the y- and z-axis of the computational cell, while in the x-direction, the free surface condition is adopted. The crystallographic directions of the Pt cell that correspond to the axes are shown in figure 1. We study the effect of a particle impact, that can be a single atom or a molecule consisting of two Pt atoms (Pt$_2$), on the free surfaces of the materials. The
surfaces of the cell are parallel to the \(<10\bar{1}\) and \(<11\bar{1}\>\) crystallographic planes of the fcc lattice and perpendicular to the direction of the flying particles. Such orientation of the cell with respect to the particles striking the surfaces is chosen along these crystallographic directions due to the distance between atoms of the lattices is the shortest, and hence, better mass transition can be expected in this case. Along the \(x\)-axis, the ideal fcc lattice has the ABAB type atom (spheres) packaging. Therefore, the third layer from the surface has the same arrangement of atoms as the first layer on the surfaces for this material. The situations, when the particles strike different sites of the surfaces are considered in the present study (indicated by numbers in figure 1).

![Figure 1.](image)

Figure 1. (a) Computational cell. Faces normal to x-axis are free surfaces. Along y and z-axes periodic boundary conditions are used. Panels (b) and (c) show crystal structure projected on \((y, z)\) and \((x, z)\) planes, respectively. Left side of the crystallite in (c) is the surface which is bombarded by single Pt atoms or by Pt\(_2\) molecules. Random atom moves along \(x\)-axis and hits the surface at a randomly chosen location (not shown). Random molecule, having random orientation in 3D space, moves along \(x\)-axis without rotation and internal oscillation and hits the surface at a randomly chosen location.

The main results are obtained for bombardment by an atom or by a molecule oriented in parallel to the surface moving exactly along a close-packed atomic row. The atom can hit into an atom of the outer atomic layer (site 1) or into an atom of the second atomic layer (site 2), while the molecule hits atoms of the both layers simultaneously. The molecular dynamics (MD) simulations are conducted using the atomic/molecular massively parallel simulator (LAMMPS) program package [22]. The embedded-atom method [23] interatomic potentials obtained by Foiles et al. [24] are employed for the simulation of the particle impact on the Pt surface. Before the modeling, the computational cell is relaxed at the zero temperature to obtain the state of the minimum potential energy. The effect of the particle impact on the mass transfer in the system is studied at 10 K for different initial velocities of the striking molecule. The simulation is performed in the NVE ensemble (constant number of atoms, volume and energy). Further, the materials are equilibrated at the corresponding temperature for 5 ps. At 10 K, the atom perturbation is very negligible and almost does not affect the results.

3. Results and discussion

The main purpose of this work is the investigation and analysis of effects arising upon the excitation of a crowdion cluster under the influence of the bombarding Pt\(_2\) molecule. The hit of this atom or molecule, shifts the surface atoms from their equilibrium positions. The resulting scenario of both excitation propagation dynamics and resulting defect structure depends on two main parameters, namely:

1) The initial velocity of the bombarding particle defines the ability of the affected atoms to overcome the potential barrier of vacancy formation and initiation of a moving soliton type object with 1D locally increased density (crowdion). If the energy provided at the initial moment is below the potential barrier threshold, one can expect the formation of a topological localized vibration mode.

2) The direction of the bombardment plays a crucial role in forming the crowdions. Our previous study [4] shows that the bombardment of a Pt\(_2\) molecule along one of the close-packed atomic rows excites a \(N=2\) crowdion when the molecule energy exceeds a certain threshold value of the initial energy. This crowdions move along only one close-packed atomic row. However, if the molecule orients in
parallel to the surface and hits atoms in the 1st and 2nd sites, then the appearance of so-called M=2 crowdion takes place. This mode is characterized by propagation along two adjacent rows simultaneously, namely, the mass and energy transport occurs in both these rows.

Now we explore the dynamics of this crowdion in two adjacent atomic rows, where the M-crowdion propagates. Figure 2 demonstrates normalized atomic displacements $x_n/a$, where $x_n$ is atomic displacement along the x axis and $a$ is the interatomic distance $a = 3.95 \text{ Å}$ at the initial velocity of the molecule equal to $v_0 = 39 \text{ Å/ps}$ during sufficiently long time (90 ps).

It is seen, that the first short-term stage of crowdion motion is supersonic. During this stage, crowdion propagates for a long distance and intensively emits its energy through phonons. Therefore, at a certain time moments, the crowdions energy becomes insufficient for overcoming the potential barrier and the crowdion transforms into a common soliton with the short lifetime. At the same time, the interstitial atoms with the small but non-zero kinetic energy are in both adjacent rows. Around these atoms a new localized vibration mode is formed with the frequency above the upper limit of the phonon spectrum.

For evaluation the conditions of the appearance of an M-crowdion cluster under the influence of a bombarding molecule, we calculate distances of propagation of the excited crowdions (crowdion clusters), when the initial velocities (energies) of a bombarding molecule are varied. Besides, we compare these distances with the one of crowdions initiated by the bombarding of only one atom into site 1 and site 2. These dependencies are depicted in figure 3.

![Figure 2](image1)

**Figure 2.** Normalized atomic displacements of the atoms in the close-packed atomic row initiated by a molecule impact simultaneously on site 1 and 2 as the functions of time for a row of the 1st site (a) and for a row in the 2nd site (b). Molecule initial velocities are $v_0 = 39 \text{ Å/ps}$. Results for $T = 10\text{ K}$. Lines of different colors correspond to the displacements of different atoms.

![Figure 3](image2)

**Figure 3.** Distance traveled by crowdion initiated by bombardment of the atom (red line) hitting in the 1st site (red dots) and in the 2nd site (white dots) or the molecule (blue squares) bombarding simultaneously in the 1st and 2nd sites as the function of (a) initial velocity and (b) initial energy of atom or molecule. Results for $T = 10\text{ K}$. The plots in figure 3 show that supersonic crowdions are initiated by an atom at a noticeably lower energy. At the same time, the distance of their propagation is sufficiently short. This causes forming only quasi-1D crowdions, which are not stable in time and transform into immovable interstitial atoms. Unlike the atom bombardment, the molecule hit can lead to the excitation of an M-crowdion, which propagates in two adjacent atomic rows. Its subsonic stage is characterized by the high-level stability.
Hence, the subsonic M-crowdion cluster can exist for a very long time. For this reason, it propagates along the whole lattice despite its slow velocity. However, exceeding a certain value of the initial energy of the molecule leads to the nonperformance of the self-focusing condition of the crowdion and the M-crowdion cluster does not emerge. Only the appearance of several 1D crowdions takes place.

4. Conclusions
The effect of atom/molecule induced 1D mass transfer in a fcc crystal of Pt has been investigated by means of atomistic simulations. It has been shown that the crowdion excitation under the bombardment of a Pt atom occurs for lower values of the initial energy than for the case of Pt2 molecule hitting. At the same time, the latter can lead to forming the so-called M-crowdion cluster (M=2) in the crystal. The important features of this mode is the very long distance of propagations. Our study have shown that the subsonic M=2 crowdion passes through the whole lattice under study. The reason of this phenomenon is that the subsonic M-crowdion cluster, which forms after the supersonic stage of the crowdion motion, is characterized by great stability in comparison with the 1D subsonic crowdion. Oscillations inside the M-crowdion have a frequency higher than the top limit of the phonon band, hence, the crowdion energy cannot be dissipated into the lattice via phonons and remains almost constant in time.

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