Highly Enhanced Transport by Supersonic *N*-Crowdions

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An interstitial atom placed in a close-packed atomic row of a crystal is called crowdion. Such defects are highly mobile, they can move along the row transporting mass and energy. In the present study the concept of the classical supersonic crowdion is generalized to *N*-crowdion in which not one but *N* atoms move simultaneously at a high speed. With the help of molecular dynamics simulations for fcc Morse crystal it is demonstrated that *N*-crowdions are much more efficient in mass transport being able to propagate through larger distances having smaller total energy than the classical 1-crowdion.

Mass transport by point defects in crystalline solids is responsible for many physical processes occurring during plastic deformation,[1–7] heat treatment,[8] irradiation,[9–13] etc. Motion of vacancies is the main mechanism of thermally activated diffusion.[8] Self-interstitial atoms have higher energy and hence, their concentration in thermal equilibrium is much smaller than that of vacancies, but their role largely increases in non-equilibrium processes. Self-interstitials can be immobile[14] or mobile, when they are located in close-packed atomic rows, creating so-called crowdions.[15] Interestingly, crowdions usually have lower potential energy than immobile interstitials.[15,16] Crowdions can be at rest and they can move with subsonic or supersonic speed.[17–19] Standing or subsonic crowdions have a kink profile spanning over from a half dozen to a dozen atoms in a close-packed atomic row. Supersonic crowdions are extremely localized, with only one or two atoms moving at the same time.[19,20]

Crowdions play very important role in crystals in the relaxation processes that involve mass and energy transport.[6,21–28] Defects produced by irradiation are mainly the interstitials and vacancies. It has been shown that clusters of interstitials are highly mobile.[21–28]

Interest to the study of moving excitations in crystals was strengthened also in relation to annealing of defects deep inside germanium single crystal under surface plasma treatment[29] and to the tracks of particles reported in mica crystals.[19,30–35] As candidates for the traveling excitations in mica, discrete breathers,[36–39] crowdions[19,40,41] and quodons[42] were considered. Dynamics and collisions of supersonic crowdions in 2D lattice have been analyzed in Ref. [43]. It has been shown that supersonic crowdions and discrete breathers can carry electric charge.[44]

Direct experimental observation of crowdions moving at supersonic speed is a challenge, that is why atomistic simulations are very helpful in their study. Structure and properties of static crowdions can be investigated using first-principles simulations.[45–47] Dynamical problems are more efficiently solved with molecular dynamics method using empiric interatomic potentials.[19,48] With this approach we report here on novel type of propagating interstitials termed as *N*-crowdions.

Numerical Setup: Cartesian coordinate system is used in the simulations. We consider fcc lattice with the lattice parameter a and interatomic distance (or atom diameter) $d = a/\sqrt{2}$. As shown in **Figure 1**(a), x and y axes are oriented along $\langle 110 \rangle$ and $\langle \bar{1}10 \rangle$ close-packed directions, respectively, while z axis along $\langle 001 \rangle$ direction.

The interatomic interactions are described by the Morse pair potential

$$U(r) = D\left(e^{-2a(r-r_m)} - 2e^{a(r-r_m)}\right). \quad (1)$$

Here U is the potential energy of two atoms at a distance r apart, and a, D, r_m are the parameters. $U(r)$ has minimum at $r = r_m$, D is the depth of the potential well, and a defines the rigidity of the bond. By a proper choice of units of energy, distance, and time one can set D, r_m, and atom mass M to be equal to one. The cut-off radius is $5r_m$. The equilibrium interatomic distance is $d = 0.9014$ for $a = 4$ and $d = 0.9612$ for $a = 5$.

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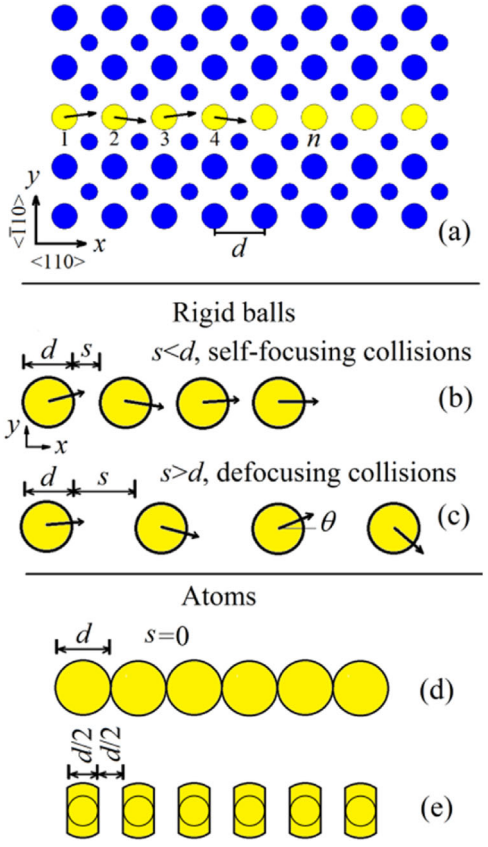

Figure 1. (a) Atoms of fcc lattice in *xy*-projection with crystallographic directions $\langle 110\rangle$, $\langle \bar{1}10\rangle$, and $\langle 001\rangle$ along *x*, *y*, and *z* axes, respectively. Circles of different size are used for atoms having different *z*-coordinate. *d* is the interatomic distance or atom diameter. Atoms in one close-packed row (shown in yellow) are numbered with index *n*. An example of initial conditions for initiation of 4-crowdion is shown: atoms from 1 to 4 have initial velocities with components $(V_0, \pm\varepsilon V_0, 0)$ with "+" for odd and "−" for even *n* and $\varepsilon \ll 1$. Schematics for the condition of self-focusing collisions in the chain of (b,c) rigid balls and (d,e) atoms.

Equations of atomic motion are integrated with the use of the Störmer method of order six with the time step $\tau = 10^{-3}$.

Thermal fluctuations are not taken into account, that is, simulations are done at 0 K.

Computational cell has dimensions $40d \times 8d \times 12d/\sqrt{2}$, which contains 3840 atoms. Periodic boundary conditions are used. Only supersonic crowdions are studied, which means that any perturbation produced by the crowdion remains in the cone behind it. This allows to use small simulation cell, moving the window containing crowdion back by 10 interatomic distances after it reaches the middle of the computational cell. With this approach, crowdion always moves in unperturbed crystal, and very long propagation distances can be efficiently simulated.

Very simple initial conditions are used to excite N-crowdions [see Figure 1(a)]. Namely, initial velocity with components $(V_0, \pm\varepsilon V_0, 0)$ is given to the atoms $n = 1, 2, \ldots, N$ in a close-packed atomic row parallel to *x* axis. Here *y*-component of the velocity is introduced with $\varepsilon \ll 1$ to check the crowdion motion stability. We take sign "+" for odd *n* and "–" for even *n*. Initial velocities of all other atoms and initial displacements of all atoms in the computational cell are equal to zero. Thus, total energy of the system is equal to the kinetic energy of the *N* excited atoms at $t = 0$,

$$T_0 = \frac{NMV_0^2}{2}, \tag{2}$$

where contribution from the lateral component of the initial velocity is neglected. Recall that atom mass $M = 1$ in our model.

Crowdion velocity will be compared to the speed of longitudinal sound along close-packed atomic row,

$$v_l = 8.3 \text{ for } a = 4, \tag{3}$$

$$v_l = 9.0 \text{ for } a = 5. \tag{4}$$

Self-Focusing Condition for the Classical 1-Crowdion: Recall that propagation of classical, supersonic 1-crowdion can be self-focusing (stable) or defocusing (unstable). Condition of self-focusing dynamics has been rigorously derived for a chain of rigid balls of diameter *d* and slit *s* between them, see Figure 1(b, c),[49] and it reads $s < d$. If this condition is satisfied, then any (small) deviation of velocity vector from the direction of the chain will decrease in successive collisions as in (b), otherwise it will exponentially grow, as in (c), where angle

$$\theta = \arctan\left(\frac{V_y}{V_x}\right) \tag{5}$$

is introduced. Importantly, for rigid balls the self-focusing condition does not depend on the velocity of ball collisions.

However, atoms are not rigid and their effective diameter depends on the collision velocity. The higher velocity the smaller is the minimal distance between centers of colliding atoms. Atom diameter in equilibrium crystal is defined as interatomic distance [see Figure 1(d)], that is why we have $s = 0$. Assuming that effective diameter of colliding atoms is equal to the minimal distance between their centers, and referring to the self-focusing condition for the rigid balls, one can formulate the self-focusing condition for atomic collisions as follows: collision velocity should not be greater than that at which minimal distance between atom centers is equal to $d/2$, see Figure 1(e). Thus, we write the self-focusing condition for collisions in the atomic chain in the form

$$d_{\min} > \frac{d}{2}. \tag{6}$$

Although this condition is not exact, we will see that for pairwise Morse interactions it works well.

Dynamics of the 1-Crowdion: We excite classical 1-crowdion by kicking one atom (with $n = 1$) in the close-packed atomic row parallel to the *x* axis with the initial velocity $((V_0, ,^{-6}V_0, ,))$. For the case of $a = 4$ we present the results in **Figure 2** for $V_0 = 17$ (left column) and $V_0 = 22$ (right column). For atoms $n = 1, \ldots, 10$, as the functions of time we plot (a,a′) normalized *x*-displacements, $\Delta x_n(t)/d$, (b,b′) *x*-component of velocity $V_{x,n}(t)$, (c,c′) normalized distances between neighboring atoms,

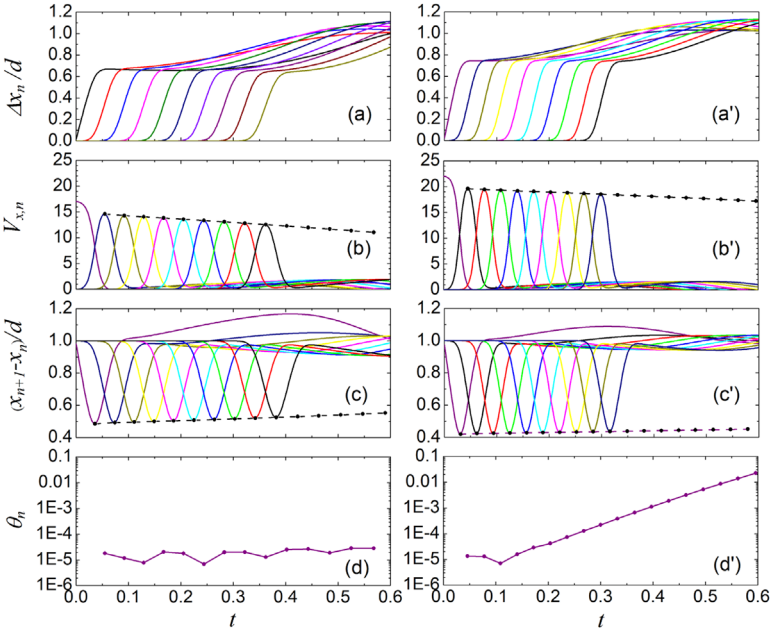

Figure 2. Dynamics of 1-crowdion excited by kicking one atom with the initial velocity $(V_0, 10^{-6}V_0, 0)$, $V_0 = 17$ (left column) and $V_0 = 22$ (right column). Atoms in the row are numbered with index n. As the functions of time shown are: (a,a′) $\Delta x_n(t)/d$, (b,b′) $V_{xn}(t)$, (c,c′) $[x_{n+1}(t) - x_n(t)]/d$ for $n = 1, \ldots, 10$. Maximal values of $V_{x,n}(t)$ in (b,b′) and minimal values of $[x_{n+1}(t) - x_n(t)]/d$ in (c,c′) are marked with dots and connected by the dashed lines. In (d,d′) θ_n is presented for the atoms in the row at time instants when $V_{x,n}$ is maximal, see in (b,b′).

$d_n(t) = [x_{n+1}(t) - x_n(t)]/d$. Maximal values of velocity in (b,b′) and minimal values of distances in (c,c′) are plotted by dots and connected by dashed lines. In (d,d′) angle θ_n defined by Eq. (5) is shown for the atoms of the row at times when velocity of n-th atom is maximal.

It can be seen from Figure 2(a,a′) that atoms in the atomic row are accelerated one after another, they cross the potential barrier located at $\Delta x_n/d = 0.5$ and move further to the position of the next atom at $\Delta x_n/d = 1$. From (b,b′) one can see that maximal velocity of n-th atom decreases with increasing n due to the energy radiation by the 1-crowdion in the form of small-amplitude running waves. From (c,c′) it can be seen that minimal distance between colliding atoms increases with propagation of the crowdion and this is due to the reduction of the collision velocity with increasing n. Minimal distance between colliding atoms satisfies the self-focusing condition Eq. (6) and collisions are indeed self-focusing since θ_n in (d) does not grow with n (note that logarithmic scale is used for the ordinate here).

Coming back to Figure 2(a,a′), it can be seen that the trajectories of the atoms toward new equilibrium positions at $\Delta x_n/d = 1$ consist of two parts, fast motion and slow motion. With increasing n, the fast motion part of the trajectory becomes shorter and crowdion motion will stop when the fast part of the trajectory does not cross the potential barrier at $\Delta x_n/d = 0.5$. One can naturally assume that the 1-crowdion would move longer if the initial velocity V_0 was larger. However, as it follows from Figure 2(d′), where $V_0 = 22$, atomic collisions become defocusing and crowdion motion is destroyed earlier.

Thus, to achieve a longer crowdion path, it is desirable to increase the energy of initial excitation without increasing initial velocity of the atoms, because at high velocities atomic collisions become defocusing. The solution is to kick not 1 but N atoms.

Dynamics of N-Crowdions: For the dynamics of N-crowdions with $N = 1$, 2, and 4, see the animated GIF files of Supporting Information, where red atoms have high kinetic energy. Dynamics of 2- and 4-crowdions initiated with $V_0 = 12$ and $\varepsilon = 10^{-6}$ is presented in **Figure 3**, left and right columns, respectively. In both cases the crowdions move in a self-focusing fashion because θ_n does not grow with n [see Figure 3 (b,b′)].

Trajectories of atoms in Figure 3(a) consist of two fast parts bringing them closer to the new equilibrium positions at $\Delta x_n/d = 1$. Trajectories of atoms in Figure 3(a′) consist of four fast parts bringing them close to the new equilibrium positions at $\Delta x_n/d = 2$, meaning that the 4-crowdion, unlike 1- and 2-crowdions, carries not one but two interstitial atoms (see dynamics of 4-crowdion in Supplemental Materials where formation of a bivacancy is seen).

Referring to Figure 2(d′), defocusing atomic collisions result in exponential divergence of angle θ in time,

$$\theta_n(t) \sim e^{\gamma t} \tag{7}$$

where γ is the critical exponent. In **Figure 4**(a) we show γ as the function of maximal velocity of n-th atom for 1- and 2-crowdions by white circles and red triangles, respectively. Note that for $V_{x,n}^{\max} < 10.5$ collisions are self-focusing since $\gamma < 0$ in this region. Note that data reported in Figure 4(a), unlike the data shown in Figures 2 and 3, are obtained not for just initialized crowdions but for crowdions during their steady motion. In Figure 4(b) normalized minimal distance between colliding atoms is shown as the function of $V_{x,n}^{\max}$. Horizontal dashed line shows that transition to self-focusing collisions takes place at

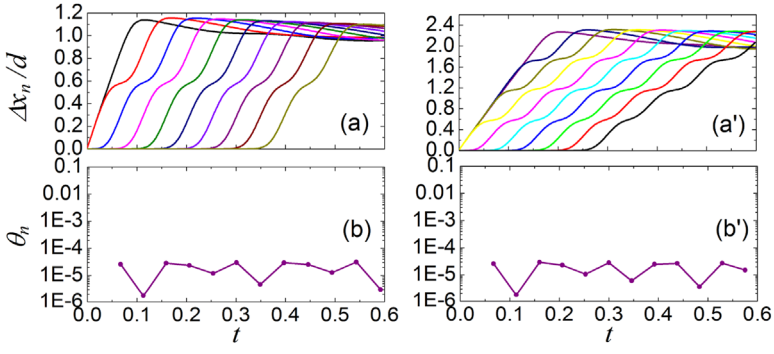

Figure 3. Same as in Figure 2(a,d) but for 2-crowdion (left column) and 4-crowdion (right column) excited with $V_0 = 12$, $\varepsilon = 10^{-6}$.

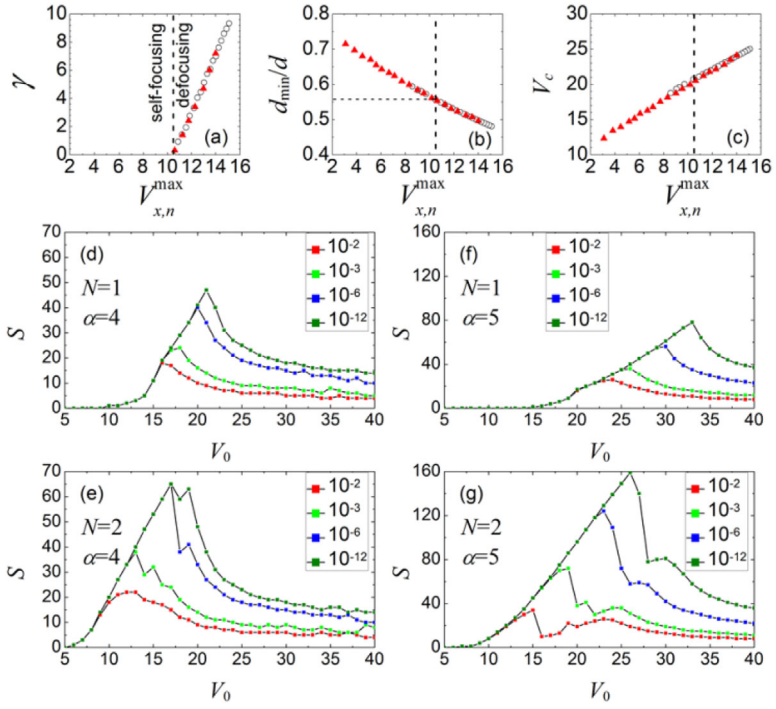

Figure 4. a–c) Results for 1-crowdion (white circles) and 2-crowdion (red triangles) for $\alpha = 4$. As the functions of the maximal velocity of n-th atom shown are: (a) critical exponent γ, (b) minimal distance between colliding atoms, and (c) crowdion velocity. Vertical dashed lines specify the border between self-focusing and defocusing collisions situated at $V_{x,n}^{\max} = 10.5$. Horizontal dashed line in (b) indicates the threshold minimal distance between colliding atoms for which self-focusing collisions take place, $d_{\min} > 0.56d$. (d-g) Distance travelled by the interstitial atom carried by (d,f) 1-crowdion and (e,g) 2-crowdion as the functions of kicking velocity V_0 for four different values of the perturbation parameter ε, as indicated in the legends. Bond stiffness parameter is (d,e) $\alpha = 4$ and (f,g) $\alpha = 5$.

$d_{\min} = 0.56d$ which is close to the idealized condition expressed by Eq. (6). In Figure 4(c) crowdion velocity is given as the function of $V_{x,n}^{\max}$. This result suggests that V_c is always greater than $V_{x,n}^{max}$ and that it is greater than the velocity of longitudinal sound.

Importantly, minimal initial velocity to initiate propagation of interstitial atom is $V_0 = 12.1$ for $N = 1$ and $V_0 = 6.7$ for $N = 2$. From Eq. (2) we find that the minimal energy required to initiate mass transfer is $T_0 = 73.2$ for $N = 1$ and $T_0 = 44.9$ for $N = 2$, which is 1.6 times smaller.

Let S be the distance travelled by the interstitial carried by a crowdion. In Figure 4(d-g), S is shown as the function of V_0 for four values of the perturbation parameter ε as indicated in the legends. In (d,f) $N = 1$ and in (e,g) $N = 2$. In (d,e) $a = 4$ and in (f, g) $a = 5$. Remarkably, 2-crowdion is able to travel through considerably larger distance than 1-crowdion and its motion can be initialized with sufficiently smaller values of the kicking velocity V_0 and smaller total energy. S increases with increasing a, which is understandable, because for larger a the interatomic potential is stiffer, minimal distance between atoms colliding with given velocity is larger, and stability condition Eq. (6) is satisfied for a larger collision velocity.

In conclusion, a new family of nonlinear excitations termed as supersonic N-crowdions has been analyzed with the help of molecular dynamics simulations for fcc Morse crystal. In contrast to classical supersonic 1-crowdion, not 1 but N atoms move at a high speed at the same time in N-crowdion. N-crowdions can travel longer distances and for their initiation smaller total energy is required than for 1-crowdion. We believe that N-crowdions can be naturally formed in the bulk of crystals under neutron irradiation or as a result of beta decay. They can also be initiated at a surface by bombardment not by single atom ions but by ionized molecules, producing not one but a series of kicks to the atoms at the crystal surface. This work should be continued by the analysis of N-crowdions in pure metals and other crystals.

Supporting Information

The Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

crystal lattice, crowdions, interstitials, mass transfer

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