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NOTE

A Method for Detecting Vacancy Diffusion in Molecular Dynamics

Molecular dynamics [1] is a powerful tool in studying solid state diffusion in metals [2]. The new many-atom potentials [3] have made the simulations of metals more quantitative, and melting transition [4], surface structures [5], and dislocation structures [6] of simple metals can be described well when compared with the experimental results. The diffusion of atoms is easy to detect during the simulation simply by following their trajectories. However, it is not as straightforward to detect vacancies and follow their jumps from one lattice site to another. This is still quite easily done in perfect crystals but the situation is more cumbersome in disordered solids, near dislocations, or in amorphous solids, where even the definition of a vacancy may become ambiguous [7, 8].

In this note we propose a simple method to detect vacancies and to follow their movements in molecular dynamics simulations. The physical idea is to use a test particle which is trapped in the vacancy and thus will follow it dynamically. In reality a rare gas atom like helium would be a good probe. In computer simulations, however, we can choose a probe which does not disturb the host solid at all. We assume that the probe is moving in a total potential caused by repulsive pairwise interactions ϕ with the host atoms positioned at $\mathbf{R}_i$:

$$V(\mathbf{r}) = \sum_i \phi(\mathbf{r} - \mathbf{R}_i). \tag{1}$$

The interaction only goes from the host atom to the probe, whereas the existence of the probe does not affect the potential felt by the host atoms. A purely repulsive potential ϕ means that a vacancy is a potential minimum for the probe. The dynamical movement of the probe is governed by the equation of motion

$$\frac{d}{dt}\mathbf{v} = \frac{1}{m_b}\mathbf{f} - \frac{\eta}{m_b}\mathbf{v}, \tag{2}$$

where m_b and $\mathbf{v}$ are the mass and the velocity of the probe, respectively, $\mathbf{f} = -\nabla V$, and η is a friction added to guarantee an adiabatic movement of the probe. The friction term is needed since the energy of the probe is not conserved (the probe has no effect on the energy of the host metal atoms). In molecular dynamics it is easy to include the probes (one or more) and to follow them by solving their equations of motion simultaneously with the equations of motion of the host atoms.

The question now is to find a potential ϕ which pulls the probe to the new vacancy when the neighbouring host atom jumps into the vacancy. A hard core potential (like Lennard-Jones) will not do, since it can push the probe to the wrong direction and possibly detrap it from the vacancy. Here we show that a Gaussian potential

$$\phi(r) = \phi_0 e^{-r^2/2\sigma^2}, \tag{3}$$

with large enough width σ always pulls the probe to the new vacancy.

The total potential $V(\mathbf{r})$ of the probe, Eq. (1), is with a good accuracy constant throughout in the perfect fcc lattice provided that the potential width σ is large enough. With $\sigma = r_{nn}$ (the nearest neighbour distance) the potential is constant with the accuracy of 1 ppm; if $\sigma = 0.5r_{nn}$ the variation in the total potential is still less than 1%. A vacancy in a perfect fcc lattice then results in an attractive Gaussian potential $-\phi(r)$ for the probe. If a neighbouring host atom starts to move towards the vacancy and, if $\sigma \geqslant r_{nn}$, the probe is immediately pulled towards that atom. This means that the purely repulsive potential can result in an effective attractive force between the probe and the moving atom. This is clearly seen in Fig. 1 which shows the potential of the probe for different positions of the neighboring host atom in the cases of $\sigma = r_{nn}$ and $\sigma = 0.8r_{nn}$. In the latter case the potential minimum is first seen to be shifted in a direction opposite to the incoming atom, but this effect is still very small.

In real simulations the host is at a finite temperature and the atoms are vibrating thermally. In addition the vacancy is relaxed. Therefore, it is better to choose σ to be slightly smaller than the nearest neighbour distance, say $\sigma = 0.8r_{nn}$. This guarantees that the potential minimum stays in the center of the vacancy and that the probe can follow the vacancy movement adiabatically. The strength of the potential ϕ_0/m_b and the friction η/m_b can be chosen so that the

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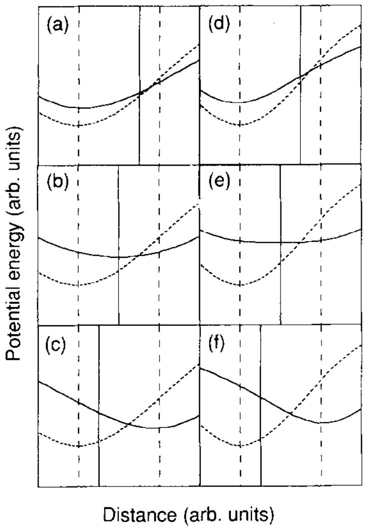

FIG. 1. Potential energy (solid curve) of the probe when one of the neighbouring atoms in an fcc lattice is moving towards the center of the vacancy. The vertical dashed lines show the positions of the vacancy and the nearest lattice site. The vertical solid line shows the site of the moving atom. The dashed curve in each figure is the potential of the probe in the original undisturbed vacancy. In (a), (b), and (c) $\sigma = r_{nn}$, in (d), (e), and (f) $\sigma = 0.8r_{nn}$.

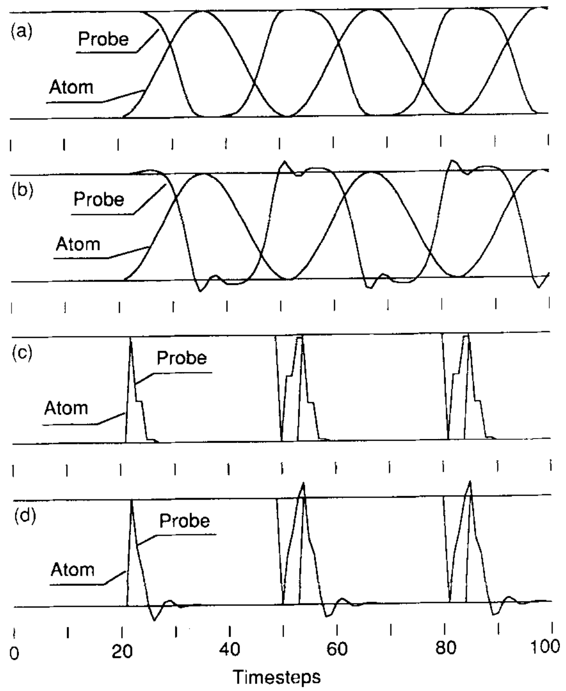

FIG. 2. Dynamics of the probe in an fcc lattice with a vacancy. In (a) and (b) the neighbouring atom starts to move sinusoidally between the vacancy center and its original position at the timestep 20. In (c) and (d) the atom makes sudden jumps between the vacancy and its original site. $\phi_0/m_b = r_{nn}/dt^2$. In (a) and (c) $\eta/m_b = 2/dt$ and $\sigma = r_{nn}$. In (b) and (d) $\eta/m_b = 1.5/dt$ and $\sigma = 0.8r_{nn}$.

probe follows the movement of the vacancy adiabatically as demonstrated in Fig. 2 for an fcc lattice where only one atom is moving: the nearest neighbour of the vacancy moves into and out of the vacancy. In (a) and (b) the atom moves sinusoidally between the two sites and the movement of the probe is followed. In (c) and (d) the response of the probe to extreme steplike jumps is shown. It is seen that by choosing $\phi_0/m_b = r_{nn}/dt^2$ (dt being the timestep) and $\eta/m_b = 2/dt$ the probe follows practically adiabatically the potential minimum.

By using the test particle the trajectory of the vacancy can be easily followed in molecular dynamics. This is especially beneficial in studying diffusion of vacancies in disordered systems, say near dislocation core, where the atoms or the vacancy are not bound to be close to the sites defined by a lattice.

The potential energy of the probe goes over a maximum when the vacancy makes a jump. By counting the maxima the total number of jumps can be determined. However, care should be taken to choose the potential parameters so that similar maxima are not obtained, for example, by a breathing movement of the atoms around the vacancy.

In amorphous solids, the usual methods of defining and detecting vacancies are the cavity analysis and the calculation of the local atomic stresses [7, 8]. This note suggests an alternative way of defining the vacancy as a deep enough minimum in the total potential of the probe. The relatively large width of the Gaussian potential means that only of the order of one sampling point per atom would be needed to observe the vacancies.

The test particles can also be used for detecting interactions between vacancies. We can choose the test particles to have a mutual interaction which is the same as the potential provided by the host atoms. Then, for example, in divacancies two test particles would be within a nearest neighbour distance from each other.

In conclusion, we propose that the vacancies can be observed and the vacancy diffusion can be followed in molecular dynamics using a test particle which has a repulsive Gaussian interaction with the host atoms.

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M. MANNINEN
H. HÄKKINEN
Department of Physics
University of Jyväskylä
SF-40351 Jyväskylä, Finland