Technical Notes

Kinetic Monte Carlo simulations of single screw dislocation motion in W

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Abstract

This document explains several developments needed for the screw dislocation kMC model.

1 Elastic energy of a piecewise kinked dislocation

The elastic energy of kinked dislocation of arbitrary shape needs to be computed piecewise, adding the contributions from all the dislocation segments. These contributions comprise self-energies and interaction energies. These can be calculated using non-singular linear elasticity and are given below.

1.1 Self-energy of a straight dislocation segment

The non-singular expression for the self-energy of a straight dislocation segment $\mathbf{m}$ defined by endpoints $\mathbf{x}_1$ and $\mathbf{x}_2$, and Burgers vector $\mathbf{b}$ is:

$$W_{self}(\mathbf{m}) = \frac{\mu}{4\pi(1-\nu)} \left\{ \left(b^2 - \nu(\mathbf{b}\cdot\mathbf{t})^2\right) L \ln\left[\frac{L_a + L}{a}\right] - \frac{3-\nu}{2}(\mathbf{b}\cdot\mathbf{t})^2(L_a - a) \right\} \qquad (1)$$

where

$$L = \|\mathbf{x}_2 - \mathbf{x}_1\|$$

$$\mathbf{t} = \frac{\mathbf{x}_2 - \mathbf{x}_1}{L}$$

and

$$L_a = \sqrt{L^2 + a^2}$$

and a is the so-called *core width* over which the Burgers vector spreads.

Sometimes, when L is of the order of a, as for kink segments, the self-energy is better computed via atomistic methods.

1.2 Interaction energy between two dislocation segments

The general expression for the interaction energy of two segments $\mathbf{m}$ and $\mathbf{n}$ with, respectively, endpoints $\mathbf{x}_1$ and $\mathbf{x}_2$, and $\mathbf{x}_3$ and $\mathbf{x}_4$ is:

$$W_{int}(\mathbf{m},\mathbf{n}) = W^*(\mathbf{x}_4-\mathbf{x}_2) + W^*(\mathbf{x}_3-\mathbf{x}_1) - W^*(\mathbf{x}_4-\mathbf{x}_1) - W^*(\mathbf{x}_3-\mathbf{x}_2) \tag{2}$$

where the functional W^* takes different forms depending on the nature of the interaction. In the following, expressions for parallel and non-parallel segments are provided. In both cases, the common Burgers vector to both segments is $\mathbf{b}$.

1.2.1 Non-parallel segments

This is relevant for the interaction between kink segments and screw segments. The energy functional $W^*(\mathbf{x}) \equiv W_{np}(\mathbf{x})$ is defined as:

$$\begin{aligned} &W_{np}(\mathbf{x}) = \\ &\frac{\mu}{4\pi(1-\nu)(\mathbf{u}\cdot\mathbf{u})}\Bigg\{\mathbf{x}\cdot\ln\left[R_a+\mathbf{x}\cdot\mathbf{t}'\right]\left((A_1-A_2')\mathbf{v}'+A_3'\mathbf{u}\right)+ \\ &+\mathbf{x}\cdot\ln\left[R_a+\mathbf{x}\cdot\mathbf{t}\right]\left((A_1-A_2)\mathbf{v}+A_3\mathbf{u}\right)+A_4R_a+ \\ &+\frac{(A_1-A_5)\left[2(\mathbf{x}\cdot\mathbf{u})^2+(\mathbf{u}\cdot\mathbf{u})a^2\right]}{\sqrt{(\mathbf{x}\cdot\mathbf{u})^2+(\mathbf{u}\cdot\mathbf{u})a^2}}\arctan\left\{\frac{(1+\mathbf{t}\cdot\mathbf{t}')R_a+\mathbf{x}(\mathbf{t}+\mathbf{t}')}{\sqrt{(\mathbf{x}\cdot\mathbf{u})^2+(\mathbf{u}\cdot\mathbf{u})a^2}}\right\}\Bigg\} \end{aligned} \tag{3}$$

where $\mathbf{t} = (\mathbf{x}_2-\mathbf{x}_1)/L_m$ and $\mathbf{t}' = (\mathbf{x}_4-\mathbf{x}_3)/L_n$ are the respective line tangents ($L_m = \|\mathbf{x}_2-\mathbf{x}_1\|$ and $L_n = \|\mathbf{x}_4-\mathbf{x}_3\|$), $\mathbf{u} = \mathbf{t}\times\mathbf{t}'$, $\mathbf{v} = \mathbf{u}\times\mathbf{t}$, $\mathbf{v}' = \mathbf{t}'\times\mathbf{u}$, and:

$$R_a = \sqrt{\mathbf{x}\cdot\mathbf{x}+a^2}$$

$$A_1 = (1+\nu)(\mathbf{b}\cdot\mathbf{t})(\mathbf{b}'\cdot\mathbf{t}')$$

$$A_2 = (b^2+(\mathbf{b}\cdot\mathbf{t})^2)(\mathbf{t}\cdot\mathbf{t}')$$

$$A_2' = (b^2+(\mathbf{b}\cdot\mathbf{t}')^2)(\mathbf{t}\cdot\mathbf{t}')$$

$$A_3 = 2(\mathbf{b}\cdot\mathbf{u})(\mathbf{b}\cdot\mathbf{v})\frac{\mathbf{t}\cdot\mathbf{t}'}{\mathbf{u}\cdot\mathbf{u}}$$

$$A_3' = 2(\mathbf{b}\cdot\mathbf{u})(\mathbf{b}\cdot\mathbf{v}')\frac{\mathbf{t}\cdot\mathbf{t}'}{\mathbf{u}\cdot\mathbf{u}}$$

$$A_4 = ((\mathbf{b}\cdot\mathbf{t})(\mathbf{b}\cdot\mathbf{v})+(\mathbf{b}\cdot\mathbf{t}')(\mathbf{b}\cdot\mathbf{v}'))(\mathbf{t}\cdot\mathbf{t}')$$

$$A_5 = 2\left(\mathbf{b}\times\mathbf{u}\right)^2\frac{\mathbf{t}\cdot\mathbf{t}'}{\mathbf{u}\cdot\mathbf{u}}$$

where $b = \|\boldsymbol{b}\|$. These expressions simplify significantly for perpendicular segments.

1.2.2 Interaction energy between two parallel segments

This interaction includes the interaction of segments of pure screw character with one another and the interaction of kink segments of the same kind with one another. As above, the Burgers vector is assumed to be the same for all segments. The interaction energy functional has the form $W^*(\mathbf{x}) \equiv W_{\parallel}(\mathbf{x})$:

$$W_{\parallel}(\mathbf{x}) = \frac{\mu}{4\pi(1-\nu)} \Bigg\{ \left[2b(\mathbf{b}\cdot\mathbf{x}) - b^2(\mathbf{t}\cdot\mathbf{x})(3-\nu)\right] \ln\left\{R_a + \mathbf{t}\cdot\mathbf{x}\right\} + R_a b^2(2-\nu) + \\ - \frac{R_a}{2} \frac{(\mathbf{b}\cdot\mathbf{x} - b\mathbf{t}\cdot\mathbf{x})^2 - a^2b^2(\nu-1)}{R_a^2 - (\mathbf{t}\cdot\mathbf{x})^2} \Bigg\} \tag{4}$$

where $\mathbf{t}$ is the common line tangent to both segments.

From Sections 1.1 and 1.2, the total elastic energy for a dislocation discretized into N segments is then:

$$E = \sum_i^N \left\{ W_{self}^i + \sum_{j>i}^N W_{int}^{ij} \right\} \tag{5}$$

The problem of computing the total elastic energy is then $\mathcal{O}\left(\frac{N^2}{2}\right)$. Later, it will be discussed how to reduce it to $\mathcal{O}(N)$. When using periodic boundary conditions, eq. 5 must include periodic image contributions. This will also be dealt with later.

2 Stress tensor from a dislocation segment

In the non-singular elastic formulation, the stress tensor at a point $\boldsymbol{x}$ from a straight dislocation segment defined by endpoints $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ and Burgers vector $\boldsymbol{b}$ is:

$$\boldsymbol{\sigma_d}(\boldsymbol{x}) = \boldsymbol{T}(\boldsymbol{x}-\boldsymbol{x}_1) - \boldsymbol{T}(\boldsymbol{x}-\boldsymbol{x}_2), \tag{6}$$

where the function $\boldsymbol{T}$ is defined as:

$$\begin{aligned} &\boldsymbol{T}(\boldsymbol{x}) = \\ &\frac{\mu}{4\pi(1-\nu)} \Big\{ \left[(\boldsymbol{x}\times\boldsymbol{b})\cdot\boldsymbol{t}\right] \left[A_1(\boldsymbol{x}\otimes\boldsymbol{x}) + A_2(\boldsymbol{t}\otimes\boldsymbol{x} + \boldsymbol{x}\otimes\boldsymbol{t}) + A_3(\boldsymbol{t}\otimes\boldsymbol{t}) + A_4\boldsymbol{I}\right] \\ &+ A_5\left[(\boldsymbol{x}\times\boldsymbol{b})\otimes\boldsymbol{t} + \boldsymbol{t}\otimes(\boldsymbol{x}\times\boldsymbol{b})\right] + A_6\left[(\boldsymbol{t}\times\boldsymbol{b})\otimes\boldsymbol{x} + \boldsymbol{x}\otimes(\boldsymbol{t}\times\boldsymbol{b})\right] \\ &+ A_7\left[(\boldsymbol{t}\times\boldsymbol{b})\otimes\boldsymbol{t} + \boldsymbol{t}\otimes(\boldsymbol{t}\times\boldsymbol{b})\right] \Big\} \end{aligned} \tag{7}$$

where

$$\boldsymbol{t} = \frac{\boldsymbol{x}_2 - \boldsymbol{x}_1}{\|\boldsymbol{x}_2 - \boldsymbol{x}_1\|}$$

$$A_1 = -\frac{\boldsymbol{x}\cdot\boldsymbol{t}\left[3R_a^2 - (\boldsymbol{x}\cdot\boldsymbol{t})^2\right]}{(R_a^2 - (\boldsymbol{x}\cdot\boldsymbol{t})^2)^2 R_a^3}$$

$$A_2 = R_a^{-3} - (\boldsymbol{x}\cdot\boldsymbol{t})A_1$$

$$A_6 = -\frac{(\boldsymbol{x}\cdot\boldsymbol{t})A_1}{R_a(R_a^2 - ((\boldsymbol{x}\cdot\boldsymbol{t})A_1)^2)}$$

$$A_3 = -R_a^{-3}\boldsymbol{x}\cdot\boldsymbol{t} + A_6 + (\boldsymbol{x}\cdot\boldsymbol{t})^2 A_1$$

$$A_4 = A_6 + a^2 A_1$$

$$A_5 = (\nu - 1)(A_6 + \frac{a^2}{2} A_1)$$

$$A_7 = \frac{\nu}{R_a} - (\boldsymbol{x} \cdot \boldsymbol{t}) A_6 - \frac{a^2(1-\nu)}{2} A_2$$

and $\boldsymbol{I}$ is the identity tensor.

As for the energies, the total stress tensor at a point $\boldsymbol{x}$ from a dislocation discretized into N segments is then:

$$\boldsymbol{\sigma}(\boldsymbol{x}) = \sum_{i}^{N} \boldsymbol{\sigma}_i(\boldsymbol{x}) \tag{8}$$

Computing the total self stress along the dislocation is then $\mathcal{O}\left(\frac{N^2}{2}\right)$ as well. Computing it at a specific location (solute atom, one dislocation segment) is $\mathcal{O}(N)$. When using periodic boundary conditions, this equation must also include periodic image contributions, as for the energy, which is treated in Section 6.

3 Free energy of a double kink

The nucleation rate of a kink pair can be defined as:

$$j_{kp} = \nu_0 \exp\left\{-\frac{\Delta F_{kp}}{2kT}\right\} \tag{9}$$

where ν_0 is an attempt frequency, and ΔF_{kp} is the (Gibbs) free energy difference resulting from the nucleation of an *embryonic* kink pair, i.e. one with the minimum lattice separation. The $\frac{1}{2}$ factor arises from the fact that it is only necessary to take the dislocation to the activated state (saddle point) to achieve a transition. As we shall see, this is only appropriate for cases where the free energy landscape is symmetric about the midpoint of the reaction coordinate. In the more general case, this landscape is not symmetric and the energies must be computed up to the relevant limits. In this section we calculate all the contributions to ΔF_{kp} without assuming symmetric free energy landscapes. The free energy can be defined as:

$$\Delta F_{kp} = \Delta H - T\Delta S = \sum_i \Delta E_i - \Delta W_m - T\Delta S$$

where ΔH is the enthalpy, ΔE_i are the different contributions to the internal energy difference, W_m is the work done by the applied stress, T the temperature and ΔS the entropy. Let us address each of these one by one in the following sections.

3.1 Contributions to the internal energy

Here we consider only two contributions to the internal energy, namely, the elastic energy and the *substrate* energy. There is a third contribution –the core energy– that is not symmetric with respect to the kink sense, but we ignore this contribution here. From Section 1, the elastic energy of a double kink as the energy difference between the dislocation in the state prior to a kink pair being nucleated $E(\mathbf{i})$, and that containing the new kink pair $E(\mathbf{j})$:

$$\Delta E_{el} = E(\mathbf{j}) - E(\mathbf{i})$$

where $E(\mathbf{i})$ and $E(\mathbf{j})$ are computed using eq. 5.

For its part, the substrate energy reflects the lattice resistance to the nucleation of a kink pair in the form of a periodic energy landscape $V_p(x)$ (for simplicity, in his section we assume that x and y are the coordinates perpendicular and parallel to the screw direction on the plane $\boldsymbol{n}$ of the kink pair). The dislocation must overcome this landscape in order to get over to the next periodic energy minimum. The substrate energy is defined as:

$$\Delta E_s = \int_{\mathbf{i}}^{\mathbf{j}} V_p(x) dl$$

where dl is the differential line element that runs from state $\mathbf{i}$ to state $\mathbf{j}$. This integral can be broken into two kink segments and one straight segment separating them. If we define $V_p(x)$ as a sinusoidal function

$$V_p(x) = E_p \sin \frac{\pi x}{h}$$

where E_p is the amplitude, also known as *Peierls* energy, and h is the kink *height*, then one can write ΔE_s as:

$$\Delta E_s = E_p w + 2 \int_0^h E_p \sin \frac{\pi x}{h} dl = E_p \left(w + \int_0^h \sin \frac{\pi x}{h} dl \right)$$

where w is the kink pair separation ($w \equiv d$, the lattice distance along the screw direction, for embryonic kinks), h is the so-called kink height, and $dl = \sqrt{dx^2 + dy^2}$. The factor of 2 reflects the fact that there are two kinks in a kink pair. To solve this integral, one need specify the line equation for a kink segment and use it to eliminate one of the variables x or y. Alternatively, one can compute this energy using atomistic methods. For example, the energy for a kink pair separated an infinite distance has been calculated to be 1.70 eV (including elastic interactions that should be accounted for) for the MEAM potential for W.

When V_p is also a function of stress, a simple sinusoidal function may not be sufficient to describe it. In such cases, the value of E_p is the maximum amplitude of the $V_p(x, \boldsymbol{\sigma})$ function over the entire integration range (reaction coordinate), which needs to be obtained by way of atomistic methods. For subsequent sections, the point at which $V_p(x, \boldsymbol{\sigma})$ is maximum, let us call it E_p', will be denoted by x_p. Then, more generally, under a situation of applied stress:

$$\Delta E_s = E_p' d + 2 \int_0^{x_p} V_p(x, \boldsymbol{\sigma}) dl$$

where it is noted that the integration limit has changed to the point of activation. This effect has been calculated directly by atomistic calculations for W-MEAM and has been found to be quite small.

Perhaps a more efficient way to take care of the entire ΔH term is to use the following expression:

$$\Delta H = \Delta H_0 \left(1 - \text{signof}(\sigma_{\text{RSS}}) \sqrt{\frac{|\sigma_{\text{RSS}}|}{\tau_{\text{P}}}} \right)^{1.25} \tag{10}$$

where:

$$\Delta H_0 = 1.70 \text{ eV}$$

$$\tau_P = 3.2 \text{ GPa}$$

and σ_{RSS} will be defined in next section. Equation 10 is from a model that captures the correct asymptotic behavior as $\sigma_{\text{RSS}} \to 0$ and $\sigma_{\text{RSS}} \to \tau_P$. One can use atomistic calculations in the intermediate stress regime to adjust eq. 10 to include all energy contributions while respecting the correct asymptotics. This will be discussed in Section 8.

3.2 Mechanical work

The mechanical work ΔW_m is obtained by calculating the work done by the Peach-Köhler force, f_{PK}, in taking the dislocation from state $\mathbf{i}$ to $\mathbf{j}$:

$$\Delta W_m(\mathbf{i} \to \mathbf{j}) = f_{PK} \Delta A(\mathbf{i} \to \mathbf{j})$$

The force per unit length can be calculated by contracting the stress and Schmid tensors:

$$f_{PK} = \boldsymbol{\sigma} : \boldsymbol{S}$$

where

$$\boldsymbol{S} = \frac{(\boldsymbol{b} \otimes \boldsymbol{n}) + (\boldsymbol{n} \otimes \boldsymbol{b})}{2}$$

The area $\Delta A(\mathbf{i} \to \mathbf{j})$ is simply the extra area created by taking the embryonic kink to the activated state, i.e. $\Delta A = x_p d$. Alternatively, this force can be obtained by calculating the resolved shear stress (RSS) on the slip system defined by slip direction $\boldsymbol{t}$ and normal $\boldsymbol{n}$. In this case, both $\boldsymbol{t}$ and $\boldsymbol{n}$ are unit vectors (the slip direction is simply $\boldsymbol{t} = \boldsymbol{b}/b$, where $b = \|\boldsymbol{b}\|$):

$$\sigma_{\text{RSS}} = \boldsymbol{t} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{n} \tag{11}$$

And then:

$$f_{PK} = b\sigma_{\text{RSS}}$$

The stress tensor $\boldsymbol{\sigma}$ at a given point $\boldsymbol{x}$ is defined as:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{app}(\boldsymbol{x}) + \boldsymbol{\sigma}_d(\boldsymbol{x}) \tag{12}$$

i.e. it contains contributions from the applied stress, typically assumed to be uniform (not dependent on $\boldsymbol{x}$), and the dislocation stress.

3.3 Entropy

The entropy is unknown but sometimes taken as $\Delta S = 3k$, where k is Boltzmann's constant.

4 Sustainable kink pair nucleation of width n

This section explains how to obtain nucleation rates of kink pairs of prescribed separation. For an existing kink pair of width w, the change in energy associated with going from state w to state $(w+1)$ (i.e. to widen by one lattice spacing) is $\Delta F_{kp} = F_{kp}(w+1) - F_{kp}(w)$. Then, the rate for a kink pair to increase its separation by one lattice spacing, i.e. changing state $w \to w+1$ is:

$$r_+(w) = \nu_0 \exp\left[-\frac{\left(F_{kp}(w+1) - F_{kp}(w)\right)/2 + U_m \mathcal{H}(w)}{kT}\right](1 + \mathcal{H}(w)) \tag{13}$$

where U_m is the energy barrier for kink migration, which is typically quite low. Identically, the rate for a kink pair to reduce its separation by one lattice spacing or $w \to w-1$ is:

$$r_-(w) = \nu_0 \exp\left[-\frac{\left(F_{kp}(w-1) - F_{kp}(w)\right)/2 + U_m}{kT}\right](1 + \mathcal{H}(w-1)) \tag{14}$$

$\mathcal{H}(w)$ is a step function:

$$\mathcal{H}(w) = \begin{cases} 1 & w \geq 1 \\ 0 & w \leq 0 \end{cases}$$

that accounts for the fact that when the kink pair is separated by a distance larger than 1, both kinks can contribute to growth or shrinkage, and, also, than when the kink pair is embryonic, only one of the kinks can move to shrink it. The total rate to escape state w is

$$r_0(w) = r_+(w) + r_-(w),$$

while the probability to undergo the $w \to w+1$ transition is:

$$\mathcal{F}(w) = \frac{r_+(w)}{r_0(w)}$$

The rate to nucleate embryonic kinks is then the rate to go from state $0 \to 1$, i.e.

$$J(1) \equiv r_+(0) = \nu_0 \exp\left[-\frac{F_{kp}(1)}{2kT}\right]$$

where the full calculation of F_{kp} is given in Section 3. The $\frac{1}{2}$ factor again assumes that the energy landscape is a symmetric function. A more realistic description, which will be used here, is given in Section 3.

Working with embryonic kinks only is very inefficient, because when they are so close together most of them just annihilate again and the system is unchanged. The idea here is to compute the rate $J(n)$ at which double kinks of separation $n > 1$ are nucleated so that the time that it takes for a kink pair of size $w = 1$ to expand to a size of $w = n$ is already factored into the nucleation rate and CPU time does not have to be wasted sampling self-annihilation events.

$J(n)$ can be written as the rate at which embryonic kinks *survive* to expand to width n, i.e.:

$$J(n) = J(1)p_s(1 \to n),$$

where $p_s(i \to j)$ is the probability for a kink pair with $w = i$ to expand to $w = j$ before annihilating. In this context, $i \geq 1$. p_s can be written as the product of the probability to go from state $w = 1$ to state $w = 2$, times the probability to go from state $w = 2$ to state $w = 3$, and so on, times the probability to go from state $w = n-1$ to state $w = n$, i.e.:

$$p_s(1 \to n) = \prod_{k=1}^{n} p_s(k \to k+1) \tag{15}$$

To go from k to $k+1$, two things can happen: either a kink goes from k to $k+1$ directly with probability $\mathcal{F}(k)$, or the kink pair first shrinks to $k-1$ with probability $1 - \mathcal{F}(k)$. From $k-1$ the kink again can either go to k and start from there, or further shrink to $k-2$ with probability

$1-\mathcal{F}(k-1)$ and start from there, and so on and so forth. This recursive process can be written as:

$$\begin{aligned} p_s(k\to k+1) &= \mathcal{F}(k)+ \\ &+\{[1-\mathcal{F}(k)]\,p_s(k-1\to k)p_s(k\to k+1)+ \\ &+[1-\mathcal{F}(k-1)]\,p_s(k-2\to k-1)p_s(k-1\to k)p_s(k\to k+1)+ \\ &+\ldots\} \\ &= \mathcal{F}(k)+p_s(k\to k+1)\left\{\sum_{i=1}^{k}[1-\mathcal{F}(i)]\prod_{j=i-1}^{k-1}p_s(j\to j+1)\right\} \end{aligned}$$

Therefore:

$$p_s(k\to k+1)=\frac{\mathcal{F}(k)}{1-\left\{\sum_{i=1}^{k}\left\{[1-\mathcal{F}(i)]\prod_{j=i-1}^{k-1}p_s(j\to j+1)\right\}\right\}} \tag{16}$$

If one discards second-order jumps, i.e. those that take the kink back beyond state $k-1$, we arrive at the more compact expression:

$$p_s(k\to k+1)=\frac{\mathcal{F}(k)}{1-[1-\mathcal{F}(k)]p_s(k-1\to k)} \tag{17}$$

Using the initial condition $p_s(0\to 1)=0$ all the surviving probabilities can be computed recursively using eqs. 16 or 17, and plugged into eq. 15 to obtain $J(n)$.

This section gives closed-form expressions to calculate the nucleation rate of kink pairs separated by a distance nd. Because the survival probabilities can be quite low, $J(n)$ will be significantly smaller than $J(1)$, but the efficiency of the simulations will increase notably. From what I have seen, the simulations do not show a strong dependence on the choice of n, although it should not be overly large compared to the total dislocation length.

5 Efficient elastic energy updates

There are two situations where the elastic energy of the dislocation must be computed. The first instance is when the nucleation rates of embryonic kinks on every available segment need to be calculated. The second one is when an event (either kink pair nucleation or kink propagation) is executed and the elastic energy of the resulting dislocation needs to be updated. We treat those two separately below.

5.1 Efficient calculation of nucleation rates

As shown above, the cost to compute the elastic energy of a given state of the dislocation line scales as $\mathcal{O}(N^2)$. Computing the nucleation rate for each segment along the line during each Monte Carlo step requires that the energy of N different states be calculated, which results in an $\mathcal{O}(N^3)$ process (N states times the cost of calculating the energy of each state, which is N^2). This obviously is prohibitive computationally. However, it turns out that, from a given reference state whose elastic energy is known, the changes in elastic energy due to an embryonic kink pair nucleated on a given segment is simply equal to the interaction energy of that unit loop with all the other N segments in the line. The interaction energy of the loop consists of calculating the

interaction energies of each of the four loop sides with each of the N segments of the dislocation line. This corresponds to N $\mathcal{O}(1)$ processes. Because this has to be done for each available nucleation site, of which there are N, the total cost of this calculation is $\mathcal{O}(N^2)$. This reduces the order of magnitude of the computational cost by one.

5.2 Elastic energy updates of the reference state

Once an event is selected and executed, updating the total elastic energy of the dislocation is simply a matter of summing the self-energy of the corresponding embryonic loop plus the work required to insert that loop in the stress field of the parent dislocation:

$$\Delta E_{el} = E^{self}_{\text{loop}} + W^{\sigma}_{\text{loop}} \tag{18}$$

The calculation of E^{self}_{loop} is a $\mathcal{O}(1)$ process because the self-energy of the loop involves the calculation of four segment self-energies plus six interaction energies (cf. Section 1). For this calculation, the line sense of the loop must coincide with that of the original dislocation.

For its part, the mechanical work to insert the loop can be calculated assuming a cartesian reference system with z along the screw direction, y parallel to the glide plane normal, and x parallel to the reaction direction. For an infinite straight screw dislocation along the z axis with $\boldsymbol{b} \equiv (0, 0, b)$, the non-singular solution for the stress field is:

$$\sigma_{xz} = -\frac{\mu b}{2\pi}\frac{y}{R_a^2}\left(1 - \frac{a^2}{R_a^2}\right) \tag{19}$$

and

$$\sigma_{yz} = -\frac{\mu b}{2\pi}\frac{x}{R_a^2}\left(1 - \frac{a^2}{R_a^2}\right) \tag{20}$$

where $R_a = \sqrt{x^2 + y^2 + a^2}$ and a is the core width. The work done to create a loop in the stress field of its parent screw dislocation can be calculated from the following integral:

$$W^{\sigma}_{\text{loop}} = b \int \sigma_s(x, y) dA \tag{21}$$

where dA is the surface area differential on the glide plane for a kink pair of separation nd, i.e.:

$$dA = (nd)dx$$

and the integral can be reduced to the stress component with a x dependence only:

$$W^{\sigma}_{\text{loop}} = bd \int \sigma_{yz} dx = -\frac{\mu b^2 nd}{2\pi} \int \frac{x}{R_a^2}\left(1 - \frac{a^2}{R_a^2}\right) dx$$

whose analytical solution is:

$$W^{\sigma}_{\text{loop}} = -\frac{\mu b^2 nd}{4\pi}\left(\frac{a^2}{a^2 + x^2} + \ln\left[a^2 + x^2\right]\right)$$

Integrated over the $[0, h]$ interval, this results in:

$$W^{\sigma}_{\text{loop}} = \frac{\mu b^2 nd}{4\pi}\left(\frac{h^2}{a^2 + h^2} - \ln\left[1 + \frac{h^2}{a^2}\right]\right) \tag{22}$$

which reduces to $W^{\sigma}_{\text{loop}} \approx \frac{\mu b^2 nd}{4\pi}\left(\frac{1}{2}+\ln 2\right) = 1.19\frac{\mu b^2 nd}{4\pi}$ when $h \approx a$. The evaluation of eq. 22 is obviously a $\mathcal{O}(1)$ process as well. In reality, the stress state at each dislocation location will not be as simple as that of a infinitely-straight dislocation, and integral 21 will have to be solved numerically including all components of the stress given by eq. 12.

Now, the information from Sections 5.1 and 5.2 can be combined to make the entire calculation of rates an $\mathcal{O}(N)$ exercise. Computing the nucleation rate in one of the N dislocation segments from the last dislocation state reduces to calculating the interaction energy between each unit loop (N of them) and the loop corresponding to the last executed event. Again, this is an $\mathcal{O}(1)$ process repeated N times so that the entire calculation of the nucleation rates becomes $\mathcal{O}(N)$.

6 Using periodic boundary conditions

The use of periodic boundary conditions (PBC) affects only the calculation of the elastic energies. In principle, one must compute the interaction energy of any given segment with all the segments of the infinite array of periodic images that result from the use of PBC. The range of dislocation-dislocation interactions varies as r^{-1} and therefore no possibility of truncation exists, which makes the infinite sums divergent. However, with the fast elastic energy updates described in Section 5 only loop-loop interactions are evaluated. In that case, because the range of loop interactions decays as r^{-3}, it is shown that it is sufficient to adopt the *minimum image convention* (MIC) to have convergent sums. The MIC allows us to have each segment interact only once with the segments of the adjacent images:

$$d'_{ij} = |\boldsymbol{x}'_j - \boldsymbol{x}_i|$$

where the $'$ refers to an *image* segment and $\boldsymbol{x}'_j$ is either equal to $\boldsymbol{x}_j \pm L$. The MIC states that:

$$\text{if } d'_{ij} > \frac{L}{2}, \text{ then } d'_{ij} = \frac{L}{2} - d'_{ij}$$

In other words, segment i of the physical dislocation line interacts only once with segment j of the image dislocation lines, that which is closest to it. Assuming we compute this extra *image* elastic energy for each segment i then eq. 5 becomes:

$$E = \sum_{i}^{N}\left\{W^{i}_{self} + \sum_{j>i}^{N}\left(W^{ij}_{int} + W^{ij'}_{image}\right)\right\} \tag{23}$$

where ij' refers to the pair formed by segment i and image segment j. I don't believe there are any other equations that need to be modified, but I will check, especially eq. 18.

7 Treatment of solute interactions

7.1 Solutes in terms of stress exerted on a dislocation

A very simple way to treat solute interactions is by considering that they are point sources of dilatation with displacement field $\boldsymbol{u} \equiv (u_r, u_\theta, u_\phi)$:

$$u_r = \frac{\delta}{r^2}, \; u_\theta = u_\phi = 0$$

The dilatation δ can be obtained from the associated eigenstrain ϵ^* as:

$$\delta = \frac{\epsilon^* r_0^3}{3} \frac{1+\nu}{1-\nu},$$

or, equivalently, from the solute relaxation volume ΔV assuming very small ϵ^*:

$$\delta = \frac{\Delta V}{12\pi} \frac{1+\nu}{1-\nu}$$

The strain deriving from u_r is:

$$\varepsilon_{rr} = \frac{\partial u_r}{\partial r} = -\frac{2\delta}{r^3}$$

From isotropic linear elasticity:

$$\sigma_{ij} = \lambda \delta_{ij} \text{div } \boldsymbol{u} + 2\mu\varepsilon_{ij}$$

and

$$\text{div } \boldsymbol{u} = \frac{1}{r^2 \sin\theta} \frac{\partial (r^2 u_r \sin\theta)}{\partial r} = 0$$

Thus, $\sigma_{rr} = 2\mu\varepsilon_{rr} = -\frac{4\mu\delta}{r^3}$, or:

$$\sigma_{rr} = -\frac{4\mu\epsilon^* r_0^3}{3r^3} \frac{1+\nu}{1-\nu} = -\frac{\mu \Delta V}{3\pi r^3} \frac{1+\nu}{1-\nu} \tag{24}$$

$$\sigma_{\theta\theta} = \sigma_{\phi\phi} = \frac{\sigma_{rr}}{2} \tag{25}$$

These expressions are equally valid for a point source or a finite-sized inclusion. The problem is that for a point source, the radius r_0 is ill-defined. The two ways to do this are to compute the relaxation volume directly from DFT calculations, or to use r_0 as the atomic radius in the matrix $r_0 = \left(\frac{a_0^3}{2}\right)^{\frac{1}{3}}$ and compute the eigenstrain as:

$$\epsilon^* = \frac{a_0' - a_0}{a_0}$$

where a_0' is the (local) lattice constant around the solute atom and a_0 the matrix lattice constant. Note that, according to either definition, the dilatation may be negative for some solutes (or vacancies).

Far away from the dislocation, the solutes then exert a force on it according to their stress field. Because a screw dislocation is only sensitive to stress along the line, the effect of $\sigma_{\phi\phi}$ can be discarded. The other two components must be projected along the line for each dislocation segment. Assuming that the angle between the screw direction and the direction joining the solute atom and the dislocation segment is $\alpha = \frac{\pi}{2} + \theta'$, then the extra stress on that segment is:

$$\sigma_s = \sigma_{rr} \sin\theta' + \sigma_{\theta\theta} \cos\theta' = -\frac{4\mu\delta}{r^3} (\sin\theta' + \frac{1}{2}\cos\theta') \tag{26}$$

The angle α can be calculated from the cross product between the screw direction (represented by the Burgers vector) and $\boldsymbol{r} = \boldsymbol{r}_s - \boldsymbol{x}$, where $\boldsymbol{r}_s$ and $\boldsymbol{x}$ are the position vectors of the solute and the dislocation segment, respectively:

$$\cos\alpha = \frac{\boldsymbol{b} \cdot \boldsymbol{r}}{\|\boldsymbol{b}\| \|\boldsymbol{r}\|}$$

This must be done for every solute and every segment, i.e. it requires $N_s N$ operations (N_s is the number of solute atoms). The stress from each solute atom in eq. 26 is then added to the total stress $\boldsymbol{\sigma}$ in Section 3.2 that each segment sees.

7.2 Another method: solutes in terms of elastic interaction energies

An alternative method to treat solutes is to calculate the dislocation-solute interaction energy when both are far from one another. These *elastic* interaction energies from all the solutes in the system are then added to the elastic energy of each segment before computing the event rates. The elastic interaction energy between a dislocation and a solute atom separated by a distance $\boldsymbol{r}$ is:

$$E(\boldsymbol{r}) = -\boldsymbol{\varepsilon} : \boldsymbol{P} \tag{27}$$

where $\boldsymbol{\varepsilon}$ is the dislocation and $\boldsymbol{P}$ is the dipole force tensor, defined as:

$$P_{ij} = \sum_{k}^{n} \left[S_i^{(k)} + d_i^{(k)} \right] F_j^{(k)} \tag{28}$$

The summation in eq. 28 goes from $k = 1$ to the n neighbors of the solute atom. s denotes the perfect lattice position of a neighbor w.r.t. the solute atom, d is the displacement of the neighbor atom from its perfect lattice position due to the solute's presence, and F is the so-called *Kanzaki* force, i.e. the force exerted on a neighbor by the solute in the relaxed configuration. Atomistic calculations can be used to precharacterize $\boldsymbol{P}$ and then eq. 27 can be solved as a function of $\boldsymbol{r}$. For vacancies or solutes, all the off-diagonal terms of $\boldsymbol{P}$ and all the diagonal terms are equal (therefore only one calculation is necessary). This also means that the interaction energy with a screw segment is zero, and only non-screw segments matter. For edge dislocations, the three diagonal components are:

$$\varepsilon_{xx} = -\frac{by}{2\pi(1-\nu)} \frac{3x^2+y^2}{r^4},\ \varepsilon_{yy} = \frac{by}{2\pi(1-\nu)} \frac{x^2-y^2}{r^4},\ \varepsilon_{zz} = \nu(\varepsilon_{xx} + \varepsilon_{yy})$$

when z is along the dislocation line, x is along the glide plane normal, and $r \equiv \|\boldsymbol{r}\| = \sqrt{x^2+y^2}$.

7.3 Short range interaction

When the solute is within the reaction distance of a dislocation segment, then we cannot use the elastic (or 'long' distance) treatment used in the above subsections. Instead, we must assume that core effects are dominant and treat the dislocation and the solute as bound with a binding energy E_b (which, again, may be negative). This energy simply adds to ΔF_{kp} in eq. 9, i.e. an extra energy E_b is required for the dislocation to overcome the solute atom. In the case when a kink encounters the solute atom, the kink motion must now be treated as diffusive. That means that E_b must be added to U_m in eq. 13 if kink motion was already being considered diffusive, or the ballistic motion of a kink must be arrested whenever it encounters a solute in its path, and treated diffusively at that point. Once the kink is released from the solute, it can be treated ballistically again. The binding energy E_b must again be computed using electronic structure calculations for the solutes of interest.

7.4 Solute diffusion

The consideration of solute atoms must include their diffusion. Solutes can jump to any one of its eight nearest sites with jump rate:

$$j_s = z\nu_0 \exp\left\{-\frac{F_v}{kT}\right\} \exp\left\{-\frac{\Delta F_m}{kT}\right\} \tag{29}$$

where F_v and ΔF_m are the vacancy formation and solute migration free energies, $z = 1/8$, and ν_0 is the jump frequency. The first exponential in eq. 29 represents the local vacancy concentration, which only depends on the pressure. Since a screw dislocation has no volumetric stress field, we can assume that F_v is independent with stress. The second exponential in the equation represents the vacancy-solute exchange.

ΔF_m is defined as:

$$\Delta F_m = \Delta E_m - \Delta W_m^s - T\Delta S_m$$

Neglecting, as above, the entropic contribution, the mechanical work in this case is:

$$\Delta W_m^s = \boldsymbol{\sigma}_s : \boldsymbol{V}^*,$$

where $\boldsymbol{\sigma}_s$ is the stress tensor at the solute, which contains contributions from the applied stress and the stress field from the dislocation. The latter can be obtained as in eqs. 19 and 20, summing the contributions of each segment and using $R_a = \|\boldsymbol{r}\|$. Alternatively, we can assume an effective *straight* dislocation, where R_a in that case is equal to the distance between the solute and the effective straight line. For its part, $\boldsymbol{V}^*$ is the activation volume tensor whose components are:

$$V_{ij}^* = \frac{\partial E_m}{\partial \sigma_{ij}}$$

.

Ideally, E_m and all the V_{ij}^* can be computed using electronic structure calculations. A cheap alternative is to assume that the stress field of a screw dislocation has no volumetric components and therefore has a weak interaction with point sources of dilatation. In this fashion, the effect of the dislocation stress field on the solute migration energy is neglected.

Once eq. 29 is fully characterized, defect diffusion is carried out on equal footing with any of the other thermally activated processes we already have.

8 Model for sustainable kink pair production when kinks move ballistically

A simple model for the enthalpy of a kink pair separated a distance s_{kp} is:

$$\Delta H(s_{kp}, \sigma) = 2\Delta E_k - \sigma b h s_{kp} - \frac{\mu b^2 h^2}{8\pi s_{kp}} \frac{1+\nu}{1-\nu} \tag{30}$$

where ΔE_k is the energy of a single kink and all the other parameters in the equation are as previously defined. Using this equation, the separation at which the stress overcomes the elastic interaction plus any thermal fluctuations aiding it can be shown to be:

$$s_{kp}^* = \left(\frac{\mu k^2 T^2}{8\pi b h \sigma^3} \frac{1+\nu}{1-\nu} \right)^{1/4} \tag{31}$$

This expression is only valid at low stresses and at higher σ the partition of ΔH into elastic interaction energy, mechanical work and single kink energies is no longer valid. In such cases one must minimize the energy of incipient kink configurations over the substrate potential. However, using elasticity to do that is questionable, since kink pairs may be so close together that the

energies are all due to core effects. In such case, atomistic calculations must be used. One can substitute eq. 30 with an adjusted version of eq. 10. For example:

$$\Delta H(s_{kp},\sigma) = \Delta H_0 \left(1 - \sqrt{\frac{|\sigma|}{\tau_P}}\right)^{1.25} \left(1 + \alpha \frac{|\sigma|}{\tau_P}\right)$$

where α is a numerical constant in the range 0.4 to 0.7. The correction term does not affect the asymptotics of the enthalpy function in the two opposite limits $\sigma \to 0$ and $\sigma \to \tau_P$. The asymptotic behaviors should be preserved in $0.2\tau_P < \sigma > 0.8\tau_P$ so that within these two intervals the analytically known asymptotic solutions are preferred as the more accurate. In between, targeted atomistic simulations should be done to fit the parameter α.

9 Velocity of kinks

9.1 Approximating kink segments as short edge dislocation segments

For the dynamics of kinks in a bcc crystal, kink segments are approximated as edge segments. This is particularly valid at high stresses, where kinks resemble sharp 90° objects. However, for simplicity, we will use that approximation in the entire stress range. Then, one can study the velocity of edge dislocations using molecular dynamics calculations and extract general laws for the motion of kinks along the line. Edge dislocations move according to a viscous law of the type:

$$v(\sigma,T) = \frac{b\sigma}{B(T)} \tag{32}$$

where b is the modulus of the Burgers vector and $B(T)$ is a temperature dependent friction coefficient (in units of Pa · s). According to phonon scattering theory, B is taken to follow a power law dependence with temperature. The exponent of the power law results from a number of contributions but, for the MD simulations that we have done, it is found that a quadratic law works best:

$$B(T) = 6.9 \times 10^{-10} T^2 - 4.8 \times 10^{-8} T$$

The kink velocity can then be written as:

$$v(\sigma,T) = \frac{2.76 \times 10^{-4}\sigma}{6.9 \times 10^{-10} T^2 - 4.8 \times 10^{-8} T} \tag{33}$$

which gives the velocity in [m · s^{-1}] when σ is the resolved shear stress in MPa and T is given in K.

9.2 Explicit calculation of kink velocities

A more physical way to simulate kink mobility is by performing simulations of isolated kinks and study their dynamic properties. Generally speaking, kinks can display both mechanical driven (stress-dependent) and diffusive (stress-independent) behavior. However, in bcc metals, including W, the barrier to kink motion on {110} planes is very low and is customarily neglected. Because

of this, the classical Arrhenius expression that is typically used to describe thermally-activated diffusion can no longer be used. Instead, the kink diffusivity can be shown to be:

$$D_k = \frac{kT}{h\gamma_k} \tag{34}$$

where h is the distance between Peierls valleys and γ_k is a temperature-independent friction coefficient measured in [stress·time] units. For its part, the mechanical driven behavior can be studied as in the preceding section (eq. 32):

$$v_k = \frac{b\sigma}{B}$$

where again B is a friction coefficient in [stress·time] units.

Atomistic simulations of suitable geometric setups can be performed to obtain γ_k by mapping equation 34 to the temperature dependence of the diffusivity, obtained as:

$$D_k = \frac{d}{dt}\langle \Delta x^2 \rangle$$

with $\langle \Delta x^2 \rangle$ the mean square displacement. For its part, B is obtained by obtaining the velocity stress curve at different temperatures.

This means that the overall dynamic behavior must account for both contributions to the mobility. A way to do this is to treat kink diffusion as a Wiener process within the kMC model in the following fashion. Assuming that a time step δt has been selected within the kMC main loop, one can write the position of the kink as:

$$\delta x_k = v_k \delta t \pm \sqrt{D_k \delta t} = \frac{b\sigma}{B}\delta t \pm \sqrt{\frac{kT\delta t}{h\gamma_k}} \tag{35}$$

where the '+' or '−' in front of the second term in the r.h.s. of eq. 35 is selected at random.

Interestingly, our latest calculations using the EAM3 potential for W show that B is temperature independent, so that:

$$v_k = 3.8 \times 10^{-6}\sigma$$

gives the velocity in m/s when σ is given in Pa, and:

$$D_k(T) = 7.7 \times 10^{-7}T$$

gives the diffusivity in m^2/s when T is in K. This numbers ensure that the diffusive component is only important at high temperatures and very low stresses.