

Diffusion-accomodated rigid-body translations along grain boundaries in nanostructured materials

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Abstract

A model for the structural relaxation of grain boundaries (GBs) in nanostructured materials (NSMs) by diffusion-accommodated rigid body translations along GBs is proposed. The model is based on the results of recent computer simulations that have demonstrated that the GBs in NSMs retain a high-energy structure with random translational states due to severe geometrical constraints applied from neighboring grains (J. Appl. Phys. 78 (1995) 847; Scripta Metall. Mater. 33 (1995) 1245). The shear stresses within a GB caused by non-optimized rigid-body translations (RBTs) can be accommodated by diffusive flow of atoms along a GB. This mechanism is particularly important for low-angle and vicinal GBs, the energy of which noticeably depends on the rigid body translations. At moderate and high temperatures the model yields relaxation times that are very short and therefore GBs in NSMs can attain an equilibrium structure with optimized rigid body translations. In contrast, at room temperature the model predicts that in some metals non-equilibrium structures can be preserved for a long time, which may result in the observation of grain boundary structures different from those in coarse grained polycrystals.

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1. Introduction

Experiments show that in as-prepared nanostructured materials (NSMs) grain boundaries (GBs) are normally in a metastable, non-equilibrium state, in contrast to GBs in coarse-grained materials. For example, in powder-compacted NSMs investigated by X-ray diffraction within 10 days after preparation, approximately 10% of atoms are located on non-lattice sites and have little or no long-range order, while in the aged and annealed samples all atoms occupy lattice positions [3]. High-resolution transmission electron microscopy studies have shown that the local atomic structure of GBs in NSMs is similar to that in coarse-grained metals, except that high internal stresses and lattice distortions exist near the boundaries [4,5]. Positron life-time studies have shown the existence of free volumes associated

with GBs in NSMs prepared by different methods [6], which also indicates non-equilibrium GB structures. Annealing of NSMs results in GB relaxation toward equilibrium structures. Differential scanning calorimetric experiments show that excess energy is released during this relaxation prior to significant grain growth [7,8]. Depending on the kind of non-equilibrium structure formed under different synthesis conditions, GB structural relaxation may have different characteristic times resulting in quite different GB structures observed by a variety of experimental methods. Thus structural models of GBs in NSMs range from frozen gas-like GBs [9] to conventional GB structures typical for coarse-grained materials [10,11].

Wolf and co-authors proposed a model for the structure of GBs in NSMs that is based on the results of extensive molecular dynamics simulations [1,2,12,13]. The cited authors generated nanostructured Cu, Si and Pd by simulated quenching of a melt starting from randomly oriented seeds. This method resembles the fabrication of NSMs by crystallization from the amor-

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phous state [14]. Two types of GBs have been generated in the samples: special tilt GBs that are known to have the lowest energy in bicrystals [15] and high-energy random GBs. The authors concluded that independent of their macroscopic geometry GBs in NSMs have an amorphous atomic structure that could be described by Rosenhain's amorphous-cement model. A comparison of the GB structures in simulated nanocrystals with those in bicrystals has shown that random GBs have essentially the same structure in both samples [13], while special GBs differ drastically in rigid-body translation (RBT) states and energies [1,2]. The high-energy state of special GBs characterized by an amorphous atomic structure has been explained by the fact that the GBs in NSMs are subjected to severe geometrical constraints from neighboring grains and therefore cannot freely relax their structure by RBTs. It is well established that RBTs of grains along GBs can change the energy of vicinal GBs dramatically [15], and as experiments [16] and simulations [17] demonstrate, in bicrystals the RBTs of GBs are usually optimized. In simulated NSMs [1,2], the RBTs of GBs are random because grains grown from randomly located seeds form the boundaries. For example, energy values of 0.2 and 0.63 J m⁻² have been found for (111) tilt boundaries with non-optimized RBTs in nanocrystalline Cu [2], while the energy of a relaxed (111) twin boundary is only 0.001 J m⁻² for a Lennard–Jones potential adjusted to Cu. Additional simulated annealing at high temperatures (about one-half the melting point, $T \approx 768$ K, for nanocrystalline Cu [1,2] and 600 K for Pd [13]) has shown no signs of irreversible transformations in GBs. On the basis of this, a conclusion has been made that NSMs created by simulated quenching are in their equilibrium state. It seems, however, that at least for vicinal and low-angle GBs, the high-energy structure is a non-equilibrium configuration that can relax to a low-energy structure at elevated temperatures, when extensive diffusion is allowed.

In the present paper, we propose a simple model for the relaxation of GBs in NSMs toward equilibrium structures that correspond to GBs in bicrystals with optimized RBTs. It is assumed that this process is controlled by atomic (or vacancy) diffusion at GBs on the distances of the order of the grain size. In Section 2, we demonstrate a simplified concept at the atomic level, considering a periodic chain of nanometer-sized grains with two alternating orientations inserted in a uniformly oriented matrix, and extend this concept to a polycrystal with randomly translated grains. In Section 3, we calculate the kinetics of the translation of a single grain, two boundaries of which are in a high energy RBT configuration. In Section 4, the results are compared to simulation data from Refs. [1] and [13] and a general discussion is given.

2. A model for RBT in polycrystals

Consider a periodic chain of columnar fcc grains with a size in the nanometer range schematically illustrated in Fig. 1. This chain is composed of two types of grains delimited by a special $\Sigma = 25$ [001] (430) GB with alternating misorientations of $\theta = \pm 16.26^\circ$. The chain is embedded into an infinite uniformly oriented matrix of the same fcc crystal from which it is divided by alternating facets (210) and (310) of the tilt GB $\Sigma = 5$. Simulations and HREM observations of GBs in bicrystals have shown that for fcc metals the most stable structures of the boundaries under consideration are the ones which have no RBT with respect to the coincidence site lattice geometrical model [18–20]. Moreover, the $\Sigma = 25$ GB is decomposed into structural units of ideal lattice plane (110) and of the GB $\Sigma = 5$ (210) [18] (this

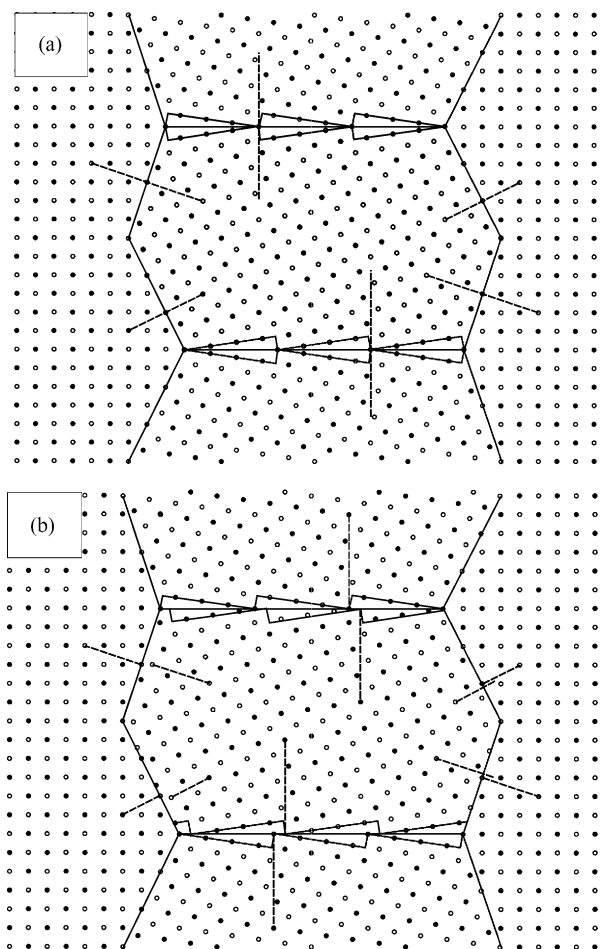


Fig. 1. A schematic representation of the structure of a periodic chain of columnar grains embedded in a uniform matrix. The grains are separated by $\Sigma = 25$ (710) tilt boundaries from each other and by $\Sigma = 5$ (310) and (210) boundaries from the matrix. In (a) all GBs have an optimized RBT and in (b) one grain of the chain is displaced to a distance Δ horizontally with respect to other grains and the matrix. Dashed straight lines indicate the positions of lattice planes normal to GBs before and after the displacement and display the RBTs along these GBs.

fact is neglected in the schematic picture of Fig. 1). To obtain a non-equilibrium GB structure with a non-optimized RBT, one of the grains of the chain is first displaced to the right some small distance. Overlapping atoms from the right-hand boundaries are then removed and added in the open regions near the left-hand boundaries (Fig. 1(b)). Upon completing this process, all GBs delimiting the displaced grain will have a non-optimized RBT. The grain will experience shear stresses along these boundaries. One can see from the figure that the forces on the grain caused by the stresses along adjacent $\Sigma = 5$ GBs approximately compensate each other along the vertical direction and give a net force which sums up with the shear force acting along the horizontal boundaries. This force tends to displace the grain back to the left. This displacement will induce compressive stress on the left-hand GBs and tensile stress on the right-hand ones. These stresses can be released by a diffusive flow of atoms from the left GBs to the right ones. If this is allowed, there are no geometrical restrictions for optimization of the RBT state of the horizontal GBs.

As an extension of the process described above, consider a NSM in which each grain is displaced a small random distance in a random direction with respect to the grain positions at which the GBs have their minimum energy structures. Accompanying the grain displacements is the filling in of the resulting open regions using atoms from the overlapping areas. This procedure results in a non-equilibrium GB structure containing shear stresses that tend to move the grains back to their initial positions. These stresses are particularly high near low-angle and vicinal GBs. If the temperature is high enough such that atomic diffusion is significant, grains can undergo a RBT accompanied by diffusion to the minimum-energy structure; this is essentially the reverse construction used to generate the non-equilibrium structure. The elemental process that controls this relaxation is a shift of a single grain due to the forces acting on its GBs, as we considered in Fig. 1. Below, we give an analytical treatment of this process.

3. Kinetics of the relaxation of non-equilibrium GBs

For a quantitative analysis, consider a single hexagon-shaped crystallite in a matrix (Fig. 2). Assume that both of the horizontal boundaries of this grain have the same non-optimized RBTs such that they experience a shear stress σ that displaces the grain to the right. The total force acting on the grain per unit length in the direction normal to the plane of the figure is equal to $2F = 2\sigma L$, where L is the length of the GBs. A shift of a grain under this force induces compressive stresses on the right-hand GBs (filled regions) and tensile stresses on

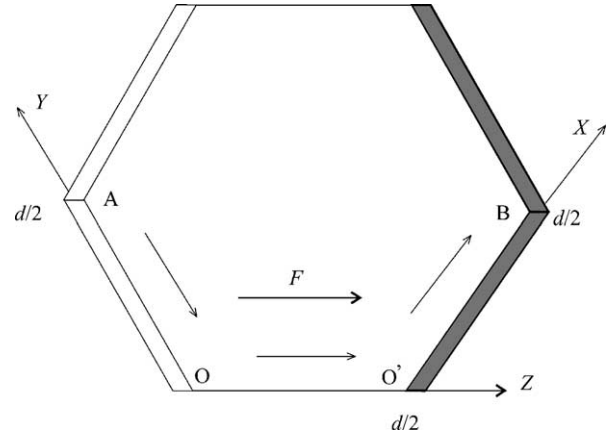


Fig. 2. A schematic rendering of the relaxation due to a RBT of a hexagonal grain. The filled regions are under compressive stress, and the open ones are under tension. The arrows indicate the directions of vacancy flow.

the left-hand boundaries (open regions). Due to the symmetry of the system, we can consider only the lower half. Correspondingly, the shear force will be equal to F . The stresses relax by a diffusive flow of atoms from the boundary $O'B$ to the boundary OA along the horizontal GB. The GB OA generates vacancies, which flow and sink on the boundary $O'B$. This process can be analyzed similar to an analysis of diffusive creep [21,22] and of the relaxation of grain boundary dislocation systems [23].

For the present system, it is convenient to introduce three axes X , Y , and Z along the three boundaries under consideration, X along the boundary $O'B$ with an origin at O' , Y along OA with an origin at O , and Z along OO' with an origin at O . Vacancy flows along these three axes are equal to [21,22]

$$J(x) = -\frac{\delta D_b}{V_a k T} \frac{d\mu}{dx}, \quad J(y) = -\frac{\delta D_b}{V_a k T} \frac{d\mu}{dy}, \quad J(z) = -\frac{\delta D_b}{V_a k T} \frac{d\mu}{dz}, \quad (1)$$

respectively, where μ is the chemical potential for vacancies, δD_b is the GB diffusion width times the GB self-diffusion coefficient, V_a is the atomic volume, T is the absolute temperature, and k is Boltzman's constant. These flows satisfy relations that follow from the material's integrity condition:

$$\frac{dJ(x)}{dx} = -\frac{dJ(y)}{dy} = \frac{u}{V_a}, \quad \frac{dJ(z)}{dz} = 0 \quad (2)$$

where u is the rate of the material deposition on the GB OA , equal to the material elimination rate from the boundary $O'B$. Therefore, one will have the following equations for the chemical potentials:

$$\frac{d^2\mu}{dx^2} = -\frac{d^2\mu}{dy^2} = -\frac{ukT}{\delta D_b} = -K. \quad (3)$$

solutions to which are the following:

$$\mu(x) = -\frac{K}{2}x^2 + A_1x + A_2, \quad (4a)$$

$$\mu(y) = \frac{K}{2}y^2 + B_1y + B_2. \quad (4b)$$

Due to symmetry, net vacancy flows at $x = d/2$ and $y = d/2$ are equal to zero. These conditions used in Eqs. (4a) and (4b) give $A_1 = Kd/2$ and $B_1 = -Kd/2$.

The constants A_2 and B_2 can be determined from the condition of the mechanical equilibrium of the grain:

$$F \sin 60^\circ = -\int_0^{d/2} \sigma_n(x) dx = \int_0^{d/2} \sigma_n(y) dy \quad (5)$$

where $\sigma_n(x)$ and $\sigma_n(y)$ are the normal stresses acting on the boundaries OA and O'B, respectively.

Chemical potentials for vacancies can be written in a linear approximation as [21]:

$$\mu(x) = \mu_0 + \sigma_n(x)V_a, \quad \mu(y) = \mu_0 + \sigma_n(y)V_a. \quad (6)$$

Substituting Eq. (6) into Eqs. (4a) and (4b), and using the expressions for normal stresses obtained from these equations into Eq. (5), one can find for the constants A_2 and B_2 :

$$A_2 = \mu_0 - \frac{\sqrt{3}FV_a}{d} - \frac{Kd^2}{12}, \quad (7a)$$

$$B_2 = \mu_0 + \frac{\sqrt{3}FV_a}{d} + \frac{Kd^2}{12}. \quad (7b)$$

The condition of the continuity of the chemical potentials yields

$$\mu(x)|_{x=0} = \mu(z)|_{z=d/2}, \quad \mu(y)|_{y=0} = \mu(z)|_{z=0}. \quad (8)$$

Because there are no vacancy sources and sinks on the GB OZ, the derivative of the chemical potential on this GB will be constant and equal to

$$\frac{d\mu(z)}{dz} = \frac{\mu(x)|_{x=0} - \mu(y)|_{y=0}}{d/2} = -\frac{kd}{3} - \frac{4\sqrt{3}FV_a}{d^2}. \quad (9)$$

Vacancy flow on the GB OZ can then be written as:

$$J(z) = -\frac{\delta D_b}{V_a kT} \left[-\frac{kd}{3} - \frac{4\sqrt{3}FV_a}{d^2} \right]. \quad (10)$$

The boundary conditions for the vacancy flows are the following:

$$J(x)|_{x=0} = J(z)|_{z=d/2}, \quad -J(y)|_{y=0} = J(z)|_{z=0} \quad (11)$$

Using any of these conditions and the relation $K = ukT/\delta D_b$, u is given by

$$u = -\frac{24\sqrt{3}\delta D_b FV_a}{5kTd^3} \quad (12)$$

From the geometry in Fig. 2 it follows that $d\Delta \cos 30^\circ = udt$, where Δ is the displacement of the grain. Therefore, the equation for the displacement rate of the grain is

$$\frac{d\Delta}{dt} = -\frac{10 \delta D_b FV_a}{kTd^3} \quad (13)$$

For a further analysis we need to have a functional form of the shear force F or the shear stress σ on the displacement Δ . This form can be estimated from simulation studies of grain boundary sliding that provide GB energies in bicrystals as a function of the relative shift of grains. In Ref. [24], sliding along the special tilt GB $\Sigma = 5$ [001] 36.87° in aluminum was simulated. We interpolated the dependence of the excess GB energy on the sliding distance near the exact coincidence position taken from Fig. 6 of the cited paper and found that ΔE increases approximately as a square of the displacement: $\Delta E \approx \alpha \Delta^2$, where $\alpha \approx 4.7 \times 10^{18} \text{ N m}^{-4}$. To estimate the value of α for palladium, it is reasonable to assume that it is proportional to the shear modulus. As the shear modulus of palladium is about twice that of aluminum, one obtains:

$$\Delta E \approx \alpha \Delta^2 \quad (14)$$

with $\alpha = 9.4 \times 10^{18} \text{ N m}^{-4}$. Therefore, the shear force acting on a half of the grain is equal to

$$F = \frac{d}{2} \left(\frac{dE}{d\Delta} \right) = d\alpha \Delta \quad (15)$$

Substituting this into Eq. (13) and solving the equation one obtains the following relaxation law:

$$\Delta(t) = \Delta_0 \exp\left(-\frac{t}{t_{\text{rel}}}\right), \quad (16)$$

where Δ_0 is the initial value of the shift of grain with respect to the minimum energy position and the characteristic relaxation time is given by the following equation:

$$t_{\text{rel}} \approx \frac{kTd^2}{10 \delta D_b V_a \alpha}. \quad (17)$$

4. Discussion

Let us first estimate the relaxation time for nanocrystalline Cu with the grain size $d = 4.34 \text{ nm}$ simulated in Ref. [2] and Pd with the grain size $d = 8 \text{ nm}$ simulated in Ref. [13], assuming the following diffusion constants: $\delta D_{b0} = 2.35 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}$ and $Q_b = 107 \text{ kJ mol}^{-1}$ for Cu [25] and $\delta D_{b0} = 5 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}$ and $Q_b = 143 \text{ kJ mol}^{-1}$ for Pd [26]. For Cu we obtain $t_{\text{rel}} = 2 \times 10^4 \text{ s} \approx 5.7 \text{ h}$ at $T = 298 \text{ K}$ and $t_{\text{rel}} = 2 \times 10^{-5} \text{ s}$ at $T = 768 \text{ K}$,

while for Pd at $T = 298$ K $t_{\text{rel}} = 7.5 \times 10^{11}$ s = 8.5×10^6 days, and at $T = 600$ K $t_{\text{rel}} = 0.37$ s. Simulated annealing times were of the order of 100 ps for both metals [2,13] at temperatures coinciding with higher values for which the estimates have been made. The estimates show that at these temperatures the time intervals in which RBT states relax are much longer than the intervals accessible by MD simulations. Hence, no indications of the relaxation in special GBs could be observed during simulations just as reported in Ref. [2].

At room temperature t_{rel} can be relatively short or very long depending on the material. In Pd, practically no relaxation of RBTs is possible even for very small grain sizes, while nanocrystalline Cu can exhibit a significant relaxation for the smallest grain sizes. Therefore, our model predicts that as-prepared GBs preserve their non-equilibrium structure with non-optimized RBTs over a long period of time for Pd.

Crystallization used to synthesize NSMs occurs over a finite time interval and therefore GB RBTs can partially relax during processing. The extent to which this relaxation influences the final GB structure is an open question, however.

The model presented here can have an application also to nanocrystals prepared by electrodeposition, since the crystallites growing during deposition may have random locations that will result in non-optimized RBT state of GBs. Moreover, HRTEM studies have shown that small-angle GBs are quite common for NSMs produced by this method [27].

It should be noted that the GB structures in NSMs addressed by atomic simulations are as controversial as the experimental data. Van Swygenhoven et al. performed a series of molecular dynamics simulations of nanocrystals in which initial systems were constructed by filling Voronoi polyhedra with randomly oriented crystallites [28]. Visualizing the relaxed structures according to the coordination numbers of atoms, they found clear evidence for repeating units in GBs, and some GBs contained structural grain boundary dislocations. These demonstrate that the GBs have a crystalline order contrary to the results obtained by Wolf and co-workers [1,2,12,13]. This controversy was related to the method used to calculate radial distribution functions applied in Refs. [1,2,12,13] that accounts for only ‘high-energy’ atoms in GBs and might therefore lead to a conclusion on the amorphous structure.

The nanostructures simulated in Refs. [1,2,12,13], on the one hand, and in Ref. [28], on the other, might also differ physically by the extent to which the starting atomic configurations are away from equilibrium. Intuitively, random filling Voronoi polyhedra should also result in non-equilibrium GB structures with non-optimized RBTs and larger free volumes than in bicrystal boundaries. Direct energy calculations done for a few GBs presented in Ref. [28] seem to yield energy

values that are comparable to the energies of equilibrium GBs (1.1 J m^{-2} for a low-energy twin-related boundary and 1.5 J m^{-2} for a higher-energy more general GB in Ni). Quite recently, however, Van Swygenhoven and co-authors performed special studies of nanostructured Ni with non-equilibrium and equilibrium GBs [29]. The ‘equilibrium’ structure was obtained by annealing the non-equilibrium samples (as prepared by the same method of Voronoi construction) for 100 ps at 800 K. During this annealing most of the distribution of local cohesive energies for GB atoms shifted left to about $\Delta\varepsilon \approx 0.025$ eV. Relating this shift to a relaxation of GBs and assuming a GB width $\delta \approx 0.05$ nm, one can estimate the corresponding decrease in the specific GB energy $\Delta\gamma = \Delta\varepsilon\delta/V_a \approx 0.2 \text{ J m}^{-2}$. This is a fairly large amount of energy and indicates that the initial GBs were indeed in a non-equilibrium state with significantly higher energies than in annealed materials. An estimate of the RBT relaxation time according to Eq. (17) for Ni ($\delta D_{b0} = 3.5 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}$, $Q_b = 115 \text{ kJ mol}^{-1}$ [25]) at $T = 800$ K and $d = 12$ nm yields a value $t_{\text{rel}} \approx 1 \times 10^{-5}$ s that is much less than in Pd at $T = 600$ K, but is still much longer than the annealing time used in the simulations of nanocrystalline Ni. One can conclude, therefore, that the energy release during annealing in this case was only due to local re-arrangements of the GB atomic structure, and that a significant amount of the excess energy had not relaxed.

This analysis shows that a non-optimized RBT is not the only possible kind of non-equilibrium structure in NSMs. There is some disorder in the local atomic structure that is not related to the translational states of GBs. This is confirmed also by the results of X-ray diffraction studies [3], which demonstrate that the X-ray spectra from nanocrystalline Pd changes after aging for about a week, while, as shown above, RBTs in this material relax in a practically infinite time interval. Therefore, another type of relaxation processes may occur at room temperature.

At moderate temperatures (about 400 K) the relaxation due to RBT occurs in reasonable time intervals. Thus, this process can contribute to the first peak of the energy release, which is observed during DSC experiments and related to the recovery of GBs [7].

The mechanism of GB relaxation presented here is specific only for NSM materials. In coarse-grained materials RBTs can be optimized by another mechanism without the assistance of diffusion. Relative translations of the grains result in the formation of triple junction dislocations and an increase in elastic energy. However, for large grain sizes this energy will be less than the energy gain due to the translation.

Recently, Haslam et al. [30] performed molecular dynamics simulations of grain growth in nanocrystalline Pd at $T = 1400$ K and found that grain rotations and subsequent disappearance of GBs is an important

mechanism for grain growth in NSMs. Moldovan et al. [31] proposed a model for diffusion accommodated grain rotations within which the driving force is the GB energy reduction due to a decrease of their misorientation angles, and found satisfactory agreement between the calculated kinetics and the simulation results of Ref. [30]. Based on Eqs. (21)–(23) of Ref. [31], one can calculate the grain rotation rate controlled by GB diffusion for nanocrystalline Pd at $T = 600$ K and $d = 8$ nm using the diffusion data presented above. This calculation yields a value $\omega_{GB} = 0.15$ rad s⁻¹. This is a fairly large value, albeit not enough to observe the grain rotations during MD simulations. Thus, grain rotations can occur simultaneously with their rigid body translations, and these two mechanisms can constitute two modes of a unique coupled process of relaxation in NSMs. The RBT relaxation rate calculated from Eq. (17) for $T = 1400$ K is about 2 ns, which is of the same order as the simulation time used in Ref. [30]. Therefore, this process could also be observed during simulations, but it might be masked by the grain growth.

In conclusion, we presented a model by which non-equilibrium GBs in polycrystalline materials can relax toward equilibrium GB structures with optimized RBTs by a diffusive flow of atoms along the GBs. This mechanism is specific for NSMs with very small grain size and particularly important for low-angle and vicinal GBs. At moderate and high temperatures the relaxation time is very short on the engineering time scale and therefore GBs in nanocrystals can attain an equilibrium structure with optimized RBTs. In contrast, at room temperature our model predicts that non-equilibrium structures can be preserved for a long time in some materials and this may stabilize the amorphous atomic structure found in atomistic simulations [1,2].

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