

Crossover from Superdiffusive to Diffusive Mixing in Plastically Deformed Solids

P. Bellon, R. S. Averbach, S. Odunuga, Y. Li, and P. Krasnochtchekov

Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Illinois 61801, USA

A. Caro

Chemistry, Materials, and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, California 94550, USA

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We derive expressions for the effective diffusion coefficient of Richardson's pairs in plastically strained solids as a function of the pair separation distance R . We predict that a crossover from superdiffusive to diffusive mixing takes place when R becomes comparable to the coherence length of the shearing events underlying the plastic deformation. Molecular dynamics simulations on nanocrystalline and amorphous systems support this analysis, which thus provides new insight on deformation mechanisms in these systems. Superdiffusive mixing is experimentally observable by monitoring the rate of dissolution of precipitates as a function of their initial size.

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Passive markers such as dye particles have been widely used to image and analyze fluid flows [1–3] since the temporal evolution of the separation distance between pairs of markers, Richardson pairs, provides a powerful tool to distinguish diffusive, convective, and turbulent mixing in fluid flows [4]. Extensions of this analysis to solid-state flows have been mostly restricted to large-scale phenomena, such as the drift of sea ice [5,6] or the mixing of the Earth's crust by plate tectonics. In a previous work [7], we employed Richardson pairs to reveal the scale dependence of mixing by plastic deformation in crystalline solids at the nanoscale. Using molecular dynamics (MD) to study the atomic mixing forced by plastic deformation in binary mixtures, we measured the mean square relative displacement (MSRD) of atom pairs $\sigma^2(R, \Delta t)$ as a function of the pair separation distance R , where Δt denotes the time elapsed between two configurations. An effective diffusion coefficient, defined as $D_{\text{eff}}(R) = 1/12 \partial \sigma^2(R, \Delta t) / \partial \Delta t$, was found to be proportional to R for separation distances $\leq L$, where L is the size of the computational cell. This unusual dependence, which leads to superdiffusive mixing, is a simple consequence of the rate of dislocations cutting through a Richardson pair being proportional to the pair separation distance, assuming homogeneous deformation.

In this Letter, we derive an expression for the effective diffusion coefficient in the more general case of a polycrystalline solid subjected to plastic deformation, and we use the result to calculate the spreading of a point source with time. A crossover from superdiffusive to diffusive mixing occurs when the pair separation distance exceeds the characteristic coherence length of the defects responsible for plastic deformation. We show that this crossover can thus be employed to determine these lengths, which are difficult to determine by other methods, in particular, for nanocrystalline and amorphous materials. Finally, we propose an experimental procedure for measuring the superdiffusive mixing during plastic deformation.

We consider a solid of size L , deformed under constant plastic strain rate $\dot{\epsilon}$, at a temperature low enough for thermal effects to be negligible. We assume that deformation results in the shearing by a vector \mathbf{b} of disklike zones of characteristic size λ_{sh} . These zones, which we take to be circular without loss of generality, are limited by Burgers dislocations in crystals. We assume furthermore that the shearing events are not correlated in time or space, as we observe in our MD simulations. The calculation of the effective diffusion coefficient requires the knowledge of the fraction of pairs of atoms separated by R that are affected by a single shearing event, and the average shift induced in the relative position of two atoms. The latter quantity can be calculated using the Burgers equation [7], which gives the displacement field $\mathbf{u}(\mathbf{r})$ induced by the presence of a dislocation loop in an elastically isotropic solid. In this equation, we need not consider the displacement generated by the dislocation bordering the loop since this elastic contribution will disappear as other loops and dislocations form and propagate in the material. In the present context, the irreversible part of $\mathbf{u}(\mathbf{r})$ is due to the shearing in the loop plane, and is given by $\mathbf{b} \cdot \Omega / 4\pi$, where Ω is the solid angle subtended by the loop at a point \mathbf{r} . Ω can be expressed in terms of elliptic integrals, but we propose here examining the two limiting cases $R \gg \lambda_{\text{sh}}$ and $R \ll \lambda_{\text{sh}}$. When $R \ll \lambda_{\text{sh}}$, it is sufficient to consider the pairs of atoms that are intersected by the plane of the loop, since Ω becomes quickly negligible otherwise; the relative displacement for these pairs is $\approx \mathbf{b}$. Straightforward geometry considerations show that the fraction of such pairs is $\approx CR\lambda_{\text{sh}}^2 L^{-3}$, where C is a constant of order unity. The effective diffusion coefficient is thus given by

$$D_{\text{eff}}(R) = \frac{C}{12} b^2 \frac{\lambda_{\text{sh}}^2 R}{L^3} \Gamma_{\text{sh}} = \frac{C}{3\pi} b R \dot{\epsilon}, \quad (1)$$

where Γ_{sh} is the rate of formation of loops, and we used the relationship $\dot{\epsilon} = (b/L)(\pi\lambda_{\text{sh}}^2/4L^2)\Gamma_{\text{sh}}$. As observed in our

previous MD simulations, $D_{\text{eff}}(R)$ is proportional to both R and the strain rate, but independent of L . By fitting these MD results [8] with Eq. (1), we find $C = 1.20$, and we use this value in what follows.

The dependence of D_{eff} with the pair separation distance leads to a superdiffusive mixing. Indeed, consider the probability distribution $q(R, t)$ for any two passive markers, initially in an infinitesimally small point source, to be separated by a distance R at time t , in a three-dimensional solid where the shearing frequency of pairs is a linear function of their separation distance, but independent of the orientation of the pairs. Taking advantage of this symmetry and Eq. (1), the kinetic equation governing the evolution of $q(R, t)$ becomes

$$\begin{aligned} \frac{\partial q(R, t)}{\partial t} &= \frac{1}{R^2} \frac{\partial}{\partial R} R^2 3D_{\text{eff}}(R) \frac{\partial}{\partial R} q(R, t) \\ &= \frac{b\Gamma_0}{R^2} \frac{\partial}{\partial R} R^3 \frac{\partial}{\partial R} q(R, t), \end{aligned} \quad (2)$$

where $\Gamma_0 = C\dot{\epsilon}/\pi$. The solution to Eq. (2) can be obtained directly by inspection [3]

$$q(R, t) = \frac{1}{8\pi(b\Gamma_0 t)^3} \exp\left(-\frac{R}{b\Gamma_0 t}\right). \quad (3)$$

The distribution of separation distances is thus exponential, while a diffusive process would lead to a Gaussian distribution. We have tested the distribution given by Eq. (3) by kinetic Monte Carlo simulations (not shown here) of a face centered cubic crystal sheared by Burgers dislocations, as well as by MD simulations of a single crystal subjected to repeated biaxial compression, alternatively along the x , y , and z axes. For these MD simulations, we used a semiempirical potential fitted on Cu and a $(7.6\text{nm})^3$ single crystal which is deformed at 100 K by 24% in each direction per cycle and at a constant strain rate of $5 \times 10^9 \text{ s}^{-1}$, using periodic boundary conditions (see Ref. [8] for details on the simulation procedure). In such simulations, dislocations glide through the whole crystal so that $\lambda_{\text{sh}} \approx L$. For pairs that were initially first nearest neighbors, Fig. 1 shows the plot of $q(R, t)$, accumulated over 1 ns, that is 7 (x, y, z) deformation cycles. As predicted by Eq. (3), $\ln(qt^3)$ scales linearly with R/t , except for very small R/t values, which are dominated by elastic displacements. Large R values should also be excluded since they do not satisfy $R \ll \lambda_{\text{sh}}$. For fitting purposes we thus used $R \leq 25\text{\AA}$ and $R/t \geq 0.01$, and the few scattered data points with large R/t values were ignored. From the slope of the fit, one extracts a value for $b\Gamma_0$ of $3.16 \times 10^{-3} \text{ \AA/ps}$. If we use $C = 1.2$, as previously determined, and $b = 2.55 \text{ \AA}$, since deformation is dominated by the glide of correlated pairs of Shockley partial dislocations, it yields a plastic strain rate of $4.2 \times 10^9 \text{ s}^{-1}$, in very good agreement with the imposed strain rate. It follows from Eq. (3) that the average square separation distance evolves

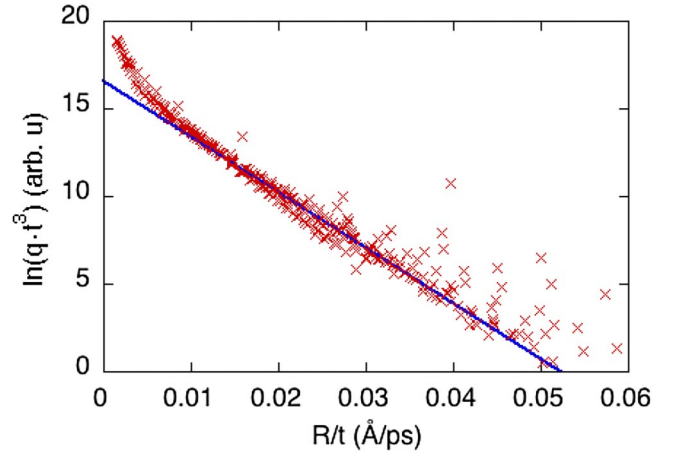


FIG. 1 (color online). The distribution of changes in pair separation distance at time t , $q(R, t)$, measured in MD simulations during cyclic deformation of single crystal Cu at 100 K is plotted versus R/t . The solid line is a fit satisfying Eq. (3) with $b\Gamma_0 = 3.16 \times 10^{-3} \text{ \AA/ps}$.

as $\langle R^2 \rangle = 12(b\Gamma_0 t)^2$, clearly revealing the superdiffusive character of the mixing.

We now turn to the other limiting case, when the pair separation distance is much larger than the characteristic size of the defects responsible for plasticity, i.e., $R \gg \lambda_{\text{sh}}$. In this case it is sufficient to consider the Richardson pairs that have one atom within a distance less than $\approx \lambda_{\text{sh}}$ from the shear loop. Indeed, as the distance d from a marker to the loop becomes larger, the solid angle behaves as $\Omega \propto d^{-2}$. Thus, if both atoms of a pair are distant from the loop by a distance exceeding λ_{sh} , the square relative displacement of the two atoms of such pairs decays as d^{-4} , whereas their number density increases only as R^2 , so that their overall contribution to the effective diffusion coefficient is negligible. The fraction of pairs that have one end in a sphere of diameter λ_{sh} bounded by the shear loop is $\pi/3\lambda_{\text{sh}}^3 L^{-3}$, and, for simplicity, we assume a constant relative displacement of $\mathbf{b}/2$. Using again the relationship between $\dot{\epsilon}$ and Γ_{sh} , the effective diffusion coefficient is calculated to be $D_{\text{eff}}^{\text{sat}} \approx \frac{1}{36} b\lambda_{\text{sh}}\dot{\epsilon}$, a value that is independent of R . Combining this last expression with Eq. (1), the crossover from superdiffusive to diffusive mixing takes place for R of the order of λ_{sh} , and thus λ_{sh} plays a role analogous to the so-called integral length scale in turbulent flows [1].

We now present a second set of MD simulations to test the above predictions, in particular, the existence of a crossover for D_{eff} . To that effect, we used a $(18.1 \text{ nm})^3$ nanocrystalline Cu system, with an initial grain size of 5 nm, which was deformed by 12% by uniaxial compression at a rate of $6 \times 10^8 \text{ s}^{-1}$ at 100 K. For a given initial pair separation R , the effective diffusion coefficient was obtained by measuring the MSRD of the corresponding atom pairs during the total simulation time. As for diffusion coefficient measurements, the MSRD should exceed a few b^2 to go beyond the ballistic regime. In addition, since

D_{eff} , by definition, depends on R , it is also required that the MSRD be small compared to R . Finally, large R values should be ignored since the corresponding pairs are affected by boundary conditions. For the present simulations, the above conditions are satisfied by imposing $10 \leq R \leq 100$ Å and using the total simulation time, ≈ 178 ps, for the calculations of the MSRD. Figure 2 shows that the effective diffusion coefficient scales linearly with R at small distances, as expected from Eq. (1), but crosses over to a constant value for larger R values. Since only one compression was carried out, atom locations were rescaled to restore the initial shape of the cell before calculating D_{eff} , thus correcting for the relative drift between atoms arising from the anisotropy of the deformation. To measure the crossover length, we fit $D_{\text{eff}}(R)$ by an exponential relaxation, and from the decay length we obtain a crossover length of ≈ 2.37 nm, i.e., half the grain size. For such small nanograin size, it has often been reported that deformation is dominated by grain boundary sliding and grain rotation [9]. We note that the formalism and assumptions used to derive Eq. (1) and related expressions can be extended to grain boundary sliding by considering a continuous distribution of elemental shear distances instead of discrete values imposed by the crystalline lattice. In evaluating the relative contributions of accommodation mechanisms, a detailed analysis of the deformation in the present case [10] shows that, while grain boundary sliding dominates, dislocation activity provides a significant contribution to the plastic strain, over 30% in steady state. The existence of a crossover at half the grain size, see Fig. 2, indicates that the coherence lengths of dislocation glide and grain boundary sliding do not exceed the grain size. For larger grain sizes, ≈ 30 nm and above, we expect that plastic deformation will be dominated by the glide and transmission of dislocations through grain boundaries, and D_{eff} would not

saturate in that case. We also note that from the slope at $R \rightarrow 0$ in Fig. 2 and Eq. (1) we obtain $b_{\text{eff}} \approx 1.33$ Å, which represents an average shear displacement of individual events resulting from dislocation glide and grain boundary sliding.

The present approach also provides new insight on the defects responsible for plastic deformation in amorphous solids. The nature and the characteristics of these so-called flow defects are still debated [11]. We performed MD simulations for a binary alloy $\text{Cu}_{50}\text{Ti}_{50}$ using semiempirical potentials [12]. A homogeneous liquid mixture equilibrated at 2000 K was quenched to 100 K at a rate of 100 K/ps to stabilize an amorphous solid. This solid was then deformed repeatedly at 100 K, at a strain rate of 5×10^9 s $^{-1}$, under uniaxial compression. Here again, D_{eff} presents a nearly linear dependence on R at small separation distances, crossing over to a constant value for $R \approx 6.5$ Å (as measured from the decay length of an exponential fit to the data). The slope of D_{eff} with R yields a direct measure of the amount of the shear in one flow defect; here, $b_{\text{am}} \approx 1.0 \pm 0.3$ Å (the large range is due to significant variations from run to run). This value is in good agreement with an analysis of the histogram of changes in pair separation distances over time, where a broad peak is observed from 1 to 1.5 Å. This distance compares favorably with the atomic displacements measured by Schuh and Lund in small amorphous clusters sheared in MD simulations [13]. The crossover length provides a direct measure of the extension of the coherence of the atomic shifts introduced by one flow defect. This number is in good agreement with the size of ≈ 1.5 nm measured by Zink *et al.*, from the correlation function of the displacement histogram [14]. We have checked that the crossover length is unchanged when the linear size of the system is doubled, from 6 to 12 nm, and when the strain rate is reduced by 1 order of magnitude.

It is generally not straightforward to use a Richardson pair analysis on experiments of plastic deformation of three-dimensional solids with nanoscale microstructures. We provide here, however, a procedure that overcomes this obstacle. Consider an initial microstructure of a binary system $A_{1-x}B_x$ that comprises pure- B precipitates, of radius R_p , in a pure- A matrix. As a consequence of the superdiffusive mixing, the precipitate dissolution rate by plastic deformation, in the absence of any other atomic transport mechanism, displays an unusual dependence on the radius of the precipitates. Indeed, the initial rate of mixing is proportional to the rate of creation of interfacial area at the matrix-precipitate interfaces. The latter rate, per volume L^3 , is the product of the number density of precipitates n_p sheared by a dislocation gliding over a distance L (for simplicity we consider here the case where slip transfer across precipitate-matrix boundaries is relatively easy, so that we can use $\lambda_{\text{sh}} = L$) times the interfacial area newly created $g2\pi R_p b$ times the frequency of dislocation glide Γ_{sh} ,

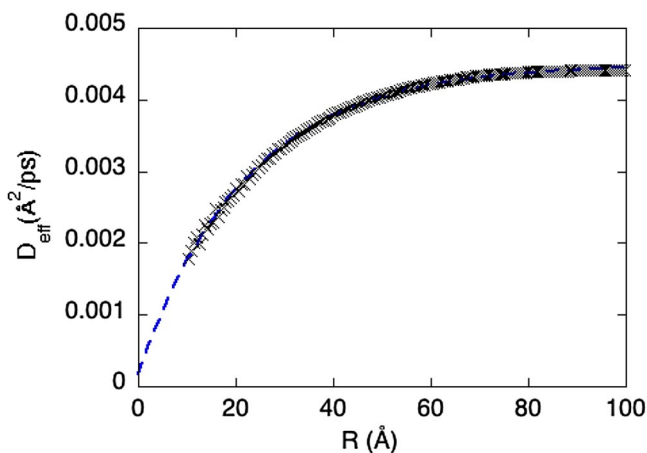


FIG. 2 (color online). Effective diffusion coefficient for the relative displacement of pairs of atoms as a function of the pair separation distance R in nanocrystalline Cu subjected to 12% compression in MD simulations. The dashed line is a fit with an exponential relaxation.

$$\frac{d(A/L^3)}{dt} = n_p \frac{2R_p}{L} g 2\pi R_p b \Gamma_{sh} = \frac{3gV_p}{R_p} \dot{\epsilon}, \quad (4)$$

where g is a geometrical factor taking into account the fact that dislocations cut the precipitates at different distances from their center. We note that an expression similar to the first equality in Eq. (4) had been derived in the past for precipitate dissolution in persistent slip bands. Equation (4) has been further simplified by introducing the volume fraction of the precipitates, $V_p = n_p 4\pi R_p^3/3$, and by taking advantage of the relationship between Γ_{sh} and the strain rate, as in Eq. (1). Finally, for the sake of comparison with experiments, we reexpress this rate in terms of the short-range order parameter of this alloy Ω . As defined by Lund and Schuh, this parameter varies from -1 for a fully decomposed state to 0 for a random alloy, to positive values for chemically ordered structures. One obtains finally

$$\frac{d\Omega}{dt} \approx \frac{3g}{4} \frac{V_p}{C_B(1-C_B)} \frac{b}{R_p} \dot{\epsilon}, \quad (5)$$

where C_B is the molar fraction of B species. The key result is that, for a given initial volume fraction of the precipitates V_p , the mixing rate is proportional to $1/R_p$. This dependence is unusual in the sense that, if these precipitates were to dissolve in the matrix by a diffusive process, the mixing rate would scale as $1/R_p^2$.

MD simulations were performed to provide further support of the unusual dissolution rate in plastically deformed solids. Figure 3 illustrates the results obtained for an A - B alloy with $x_B = 25\%$, a positive heat of mixing of

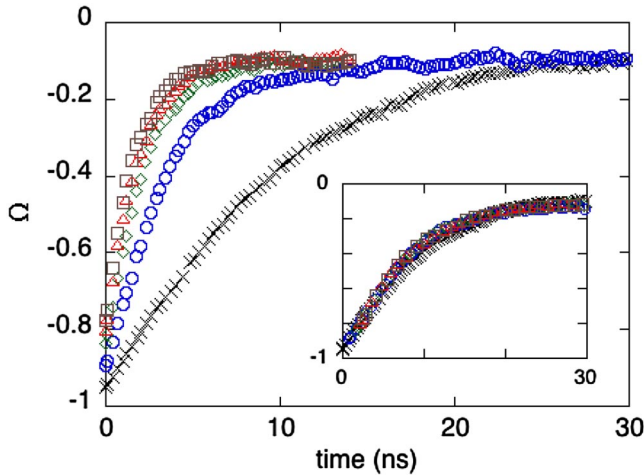


FIG. 3 (color online). Evolution of the mixing parameter Ω (see text for definition) during the dissolution of nanoprecipitates forced by biaxial compression of a crystalline $A_{75}B_{25}$ alloy in MD simulations, containing initially 1 (\times), 10 (\circ), 30 (\diamond), 50 (\triangle), and 70 (\square) pure B precipitates. The inset shows the collapse of data onto one master curve when time is rescaled as $t(R_1/R_n)^\alpha$ with $\alpha = 1.05$, where R_n is the precipitate radius for the initial configuration with n precipitates.

15.6 kJ/mol, and no lattice mismatch. The simulation cell contained 32 000 atoms and was deformed at a rate of $5 \times 10^9 \text{ s}^{-1}$ following the method used in our previous work [8], with the exception that biaxial compression is used here to suppress twinning. The simulations are run at 100 K to suppress any thermally activated atomic transport. Various initial microstructures were prepared, with the same volume fraction of precipitates, $V_p = 25\%$, but with 1, 10, 30, 50, and 70 precipitates. As illustrated by the inset of Fig. 3, the data collapse onto a single curve when a rescaled time unit $t(R_p)^{-\alpha}$ is employed. The best fit is obtained for $\alpha = 1.05$, which is in very good agreement with the value 1.0 predicted by Eq. (5). The comparison of the initial mixing rates measured from the MD results to those expected from Eq. (5) yields $g \approx 1/4$, a value consistent with the picture employed to derive Eq. (5). We note that the mixing rate given by Eq. (5) is a minimum value since we have only considered the dislocations geometrically necessary to achieve a given plastic strain. Besides fundamental interest, the scale dependence of mixing forced by plastic deformation should be relevant to materials processing, in particular, mechanical alloying, rolling, and friction stir welding, and to the evolution of tribolayers during frictional wear.

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- [1] H. Tennekes and J.L. Lumley, *A First Course In Turbulence* (MIT Press, Cambridge, MA, 1972).
- [2] B.I. Shraiman and E. D. Siggia, *Nature (London)* **405**, 639 (2000).
- [3] S. Ott and J. Mann, *J. Fluid Mech.* **422**, 207 (2000).
- [4] L.F. Richardson, *Proc. R. Soc. A* **110**, 709 (1926).
- [5] A. S. Thorndike, *J. Geophys. Res. Oceans* **91**, 7691 (1986).
- [6] D. Marsan, H. Stern, R. Lindsay, and J. Weiss, *Phys. Rev. Lett.* **93**, 178501 (2004).
- [7] J.P. Hirth and J. Lothe, *Theory of Dislocations* (Krieger, Malabar, FL, 1982), 2nd ed.
- [8] S. Odunuga, Y. Li, P. Krasnochtchekov, P. Bellon, and R. S. Averback, *Phys. Rev. Lett.* **95**, 045901 (2005).
- [9] J. Schiotz, F.D. Di Tolla, and K.W. Jacobsen, *Nature (London)* **391**, 561 (1998).
- [10] S. Odunuga *et al.* (to be published).
- [11] See, e.g., F. Spaepen, *Acta Metall.* **25**, 407 (1977); M.L. Falk and J. S. Langer, *Phys. Rev. E* **57**, 7192 (1998); J. S. Langer, *Phys. Rev. E* **70**, 041502 (2004); W.L. Johnson and K. Samwer, *Phys. Rev. Lett.* **95**, 195501 (2005).
- [12] M.J. Sabochick and N.Q. Lam, *Phys. Rev. B* **43**, 5243 (1991).
- [13] C.A. Schuh and A.C. Lund, *Nat. Mater.* **2**, 449 (2003).
- [14] M. Zink, K. Samwer, W.L. Johnson, and S.G. Mayr, *Phys. Rev. B* **73**, 172203 (2006).