Directional grain growth from anisotropic kinetic roughening of grain boundaries in sheared colloidal crystals

Shreyas Gokhale^{a,1}, K. Hima Nagamanasa^{b,1}, V. Santhosh^c, A. K. Sood^{a,c}, and Rajesh Ganapathy^{c,2}

^aDepartment of Physics, Indian Institute of Science, Bangalore 560012, India; ^bChemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; and ^cInternational Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India

Edited by James A. Warren, National Institute of Standards and Technology, Gaithersburg, MD, and accepted by the Editorial Board October 25, 2012 (received for review June 19, 2012)

The fabrication of functional materials via grain growth engineering implicitly relies on altering the mobilities of grain boundaries (GBs) by applying external fields. Although computer simulations have alluded to kinetic roughening as a potential mechanism for modifying GB mobilities, its implications for grain growth have remained largely unexplored owing to difficulties in bridging the widely separated length and time scales. Here, by imaging GB particle dynamics as well as grain network evolution under shear, we present direct evidence for kinetic roughening of GBs and unravel its connection to grain growth in driven colloidal polycrystals. The capillary fluctuation method allows us to quantitatively extract shear-dependent effective mobilities. Remarkably, our experiments reveal that for sufficiently large strains, GBs with normals parallel to shear undergo preferential kinetic roughening, resulting in anisotropic enhancement of effective mobilities and hence directional grain growth. Single-particle level analysis shows that the mobility anisotropy emerges from strain-induced directional enhancement of activated particle hops normal to the GB plane. We expect our results to influence materials fabrication strategies for atomic and block copolymeric polycrystals as well.

colloids | grain boundary migration | anisotropic grain growth

The motion and rearrangement of grain boundaries (GBs) is central to our understanding of recrystallization (1), grain growth and its stagnation (2), and superplasticity (3) in a broad class of polycrystalline materials including metals (4), ceramics (5), colloidal crystals (6), and block copolymers (7, 8). Polycrystals are pervasive as engineering materials and elucidating mechanisms that determine the structure and dynamics of their GBs continue to be a central goal of materials research (9). Advances in computer simulation methods (2, 10, 11) and experiments (12, 13) have provided substantial insights into the microscopic origins of these mechanisms. In conventional materials, nevertheless, establishing a direct link between the dynamics at the single/few atom length scale and the collective behavior of the many thousands of atoms that constitute GBs and grains poses a serious challenge (14).

A bridging of length scales is vital for grain growth studies. The key parameter in grain growth and its stagnation is the mobility of GBs, which is determined by their roughness (2, 15). Although transmission electron microscopy (TEM) is well-suited for grain growth measurements, no technique exists that can nonintrusively quantify the atomic scale roughness of buried GBs (14). These experimental shortcomings are compounded in driven polycrystals, which assume practical significance in the fabrication of functional materials via grain growth engineering (2, 7). Driven GBs (16) are thought to kinetically roughen (17), which may result in significantly enhanced mobilities (15) and influence grain growth. Further, in nanocrystalline materials, which often possess superior mechanical properties compared with their coarse-grained counterparts (18), kinetic roughening is expected to have a profound impact on mechanical behavior (16). Despite its technological

relevance, the implications of kinetic roughening for GB mobility and grain growth remain poorly understood. Although molecular dynamics simulations can model atomistic phenomena realistically, they often are limited to small system sizes (19) and short time scales (11), which may influence measurements of GB roughness (15) and predictions of grain growth laws (2, 20). Kinetic Monte Carlo simulations (21) and phase field models (22) are insensitive to microscopic details. Thus, there is a need for a complementary multiscale approach that can probe kinetic roughening and its link to grain growth in driven polycrystals.

In this work, we combined techniques in colloid science to investigate the dynamics of GBs in sheared 3D colloidal crystals over length scales spanning from the single-particle level to that of the GB network. Our single-particle resolution experiments reveal that for large oscillatory strains, boundaries with normals oriented parallel to shear are preferentially kinetically roughened. We find that the equilibrium capillary fluctuation method (CFM) allows us to extract effective mobilities, even under shear. Analysis of dynamics at the single-particle level reveals that strain-induced anisotropy in particle displacements is manifested as a preferential enhancement of the effective mobilities. Most strikingly, by imaging the GB network under shear, we show that this shear-induced anisotropy in the mobility leads to directional grain growth. Because colloid models are valuable analogs of atomic systems (23–27), insights gained from the present studies should be relevant for atomic and block copolymeric polycrystals as well.

Our system consisted of thermo-responsive size-tunable poly (*N*-isopropylacrylamide) (PNIPAm) colloids tagged with the fluorophore rhodamine 6G for confocal imaging (*Materials and Methods*). We adjusted the suspension volume fractions ϕ such that at 311 K, where the particle diameter $\sigma = 0.60\ \mu\text{m}$, $\phi < 50\%$, and the equilibrium phase is a liquid. Annealing the samples to 296 K led to particle swelling, with $\sigma = 0.95\ \mu\text{m}$, resulting in a $\phi \sim 70\%$, and the suspension crystallized into a polycrystalline state. A particular advantage of PNIPAm colloids is that they allow us to control the grain size systematically by altering the annealing rate (*SI Text* and *Fig. S1*). To mimic the nanocrystalline regime in which GB-mediated response is predominant (12, 18) and grain sizes typically are 50–200 atom diameters across, we aimed for average grain sizes of the order of 100 colloid diameters. We restricted

Author contributions: S.G., K.H.N., A.K.S., and R.G. designed research; V.S. and R.G. designed the confocal rheometer; S.G. and K.H.N. performed research; V.S. and R.G. contributed new reagents/analytic tools; S.G. and K.H.N. analyzed data; and S.G., K.H.N., A.K.S., and R.G. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission. J.A.W. is a guest editor invited by the Editorial Board.

¹S.G. and K.H.N. contributed equally to this work.

²To whom correspondence should be addressed. E-mail: rajeshg@jncasr.ac.in.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1210456109/-DCSupplemental.

Fig. 2. Shear-induced anisotropy in GB mobility. $L\langle |A(k)|^2 \rangle k^2$ vs. k for (A) $\gamma_o = 2\%$, (B) $\gamma_o = 8.3\%$, and (C) $\gamma_o = 18.3\%$ for $\text{GB}_{\parallel}$ (●) and $\text{GB}_{\perp}$ (○). (D) Stiffness Γ as a function of γ_o obtained from A–C by averaging $L\langle |A(k)|^2 \rangle k^2$ over the shaded region. (E) Mobility M and (F) reduced mobility $M^* = M\Gamma$ as a function of γ_o for $\text{GB}_{\parallel}$ (●) and $\text{GB}_{\perp}$ (○). In D–F, $\square$ corresponds to $\gamma_o = 0\%$.

as well (Fig. S6). We find that $L\langle |A(k)|^2 \rangle k^2$ is nearly a constant $\frac{k_B T}{\Gamma}$ over a decade in k , for both boundary configurations and for all γ_o . Notably, we find that Γ , obtained by averaging $L\langle |A(k)|^2 \rangle k^2$ over the shaded region (Fig. 2A–C), is preferentially lowered for $\text{GB}_{\parallel}$ (solid circles) compared with $\text{GB}_{\perp}$ (hollow circles) for $\gamma_o \geq 8.3\%$ (Fig. 2D and Fig. S5A). An anisotropic lowering of Γ for $\text{GB}_{\parallel}$ vs. $\text{GB}_{\perp}$ is a result of anisotropic enhancement in the interface roughness and is consistent with Fig. 1C–E. It is important to note that in ref. 36 Γ depends on the shear rate $\dot{\gamma}$, whereas for HAGBs we find that Γ depends strongly on γ_o (SI Text and Fig. S7).

For capillary fluctuations that decay as $\langle A(k, 0)A^*(k, t) \rangle = \langle |A(k)|^2 \rangle e^{-M\Gamma k^2 t}$, the dynamic correlation function $g_d(\tau) = \langle \Delta h(x, t) \Delta h(x, t + \tau) \rangle_{x,t} = \frac{k_B T \xi}{\Gamma} \text{erfc} \left(\frac{(\Gamma M t)^{\frac{1}{2}}}{\xi} \right)$ (SI Text, Fig. S8, and

Fig. S9A–C) yields the product $M\Gamma$ (37). Here, ξ is the lateral correlation length (38) obtained from exponential fits to the height–height correlation function $g_h(\delta x) = \langle \Delta h(x, t) \Delta h(x + \delta x, t) \rangle_{x,t}$ (Fig. S9D and E) and $\text{erfc}(t)$ is the complementary error function. Fig. S9A–C shows $g_d(\tau)$ for $\text{GB}_{\parallel}$ (solid circles) and $\text{GB}_{\perp}$ (hollow circles) for increasing γ_o . Plugging in the value of Γ (Fig. 2D), obtained earlier, into the complementary error function fits of the data (black lines in Fig. S9A–C) yields an effective shear-dependent mobility M . We find that the increase in M with γ_o for the kinetically roughened boundary, $\text{GB}_{\parallel}$ (Fig. 2E, solid circles), is more rapid compared with $\text{GB}_{\perp}$ (Fig. 2E, hollow circles) and is almost an order of magnitude larger at $\gamma_o = 18.3\%$ (Fig. S5B). It generally is believed that kinetic roughening alters GB mobilities and dictates microstructure evolution in driven polycrystals. However, even in the zero-driving force limit, a connection between roughness and mobility has been shown only in computer simulations (15) and its extension to nonzero driving forces has not been explored. By integrating fast confocal microscopy with rheology, we have shown that the shear-induced anisotropy in M is a direct consequence of preferential kinetic roughening.

Will shear-induced anisotropy in mobility, $M_{\parallel} > M_{\perp}$, lead to directional grain growth? To answer this question, we take a closer look at the mobility relation $v = M\Gamma\kappa + MP_{\text{ext}}$ (31). Focusing on the second term, one would naively expect that an anisotropy in M implies an anisotropy in v . Although it is difficult to characterize P_{ext} acting on GBs in a driven polycrystal (2), it chiefly consists of contributions from the applied bulk stress and its coupling to the elastic anisotropy in adjacent grains (39). In our experiments, we expect the driving force due to bulk stress to be zero because of the

oscillatory nature of the applied strain. Further, the driving force due to elastic anisotropy becomes significant only for grain sizes larger than about $1 \mu\text{m}$ ($\sim 3,000\sigma$) in atomic systems (39), which is much larger than the grain sizes used in our experiments ($\sim 100\sigma$). It therefore is likely that in our experiments, $P_{\text{ext}} = 0$ and hence $v = M\Gamma\kappa$. We note that with increasing γ_o , M increases (Fig. 2E) whereas Γ is found to decrease (Fig. 2D) for both $\text{GB}_{\parallel}$ and $\text{GB}_{\perp}$. Thus, in the approximation $P_{\text{ext}} = 0$, we expect an anisotropy in GB motion and grain growth only if the reduced mobility, $M^* = M\Gamma$, is itself anisotropic. Remarkably enough, Fig. 2F shows that anisotropic kinetic roughening indeed results in anisotropic-reduced mobilities with $M^*_{\parallel} > M^*_{\perp}$ at large γ_o . Although we considered a narrow range of Θ s to allow comparison across the two GB configurations, given that HAGBs exhibit qualitatively similar dynamics over a broad range of Θ s (27, 40), we expect the anisotropy in M and M^* to be a generic feature of these boundaries.

Directional Grain Growth Under Shear. Even as our single-particle resolution measurements revealed a shear-induced anisotropy in both M and M^* , to link this to grain growth it is necessary to probe GB dynamics under shear at the grain network length scale. To this end, we performed Bragg diffraction microscopy (BDM), which is the analog of TEM for colloidal crystals (41), simultaneously with rheometry (Materials and Methods, SI Text, and Fig. S2B). Here, the colloidal crystal sample, confined between the shear plates, is illuminated by a white-light source and a detector is placed at the first Bragg diffracted spot. A perfect single crystal would result in uniform intensity at the detector. For a polycrystal, however, the Bragg condition is met only by crystallites of a particular orientation, resulting in a diffraction contrast image. We note here that BDM does not yield an orientation map of the polycrystal but allows us to distinguish between low-angle GBs, which appear as arrays of discrete spots corresponding to dislocation cores, and HAGBs, which appear as continuous curves (42). A typical BDM snapshot of the colloidal polycrystal is shown in Fig. 3A, with $\text{GB}_{\parallel}$ s shown by solid lines and $\text{GB}_{\perp}$ s shown by dashed lines. Fig. 3B and C shows $\langle h(x, t) \rangle_x$ vs. t for $\gamma_o = 3.9\%$. In complete concord with results thus far, anisotropy in M and M^* indeed results in anisotropic grain growth with $v_{\parallel} > v_{\perp}$ on an average (Movie S2; see also SI Text, Fig. S10, and Movie S3). As a consistency check, we estimated the expected GB velocity by plugging in the value of M^* and assuming $\kappa = \frac{1}{d}$, where d is the average grain radius, which is ~ 100

24. Schall P, Weitz DA, Spaepen F (2007) Structural rearrangements that govern flow in colloidal glasses. *Science* 318(5858):1895–1899.
25. Ganapathy R, Buckley MR, Gerbode SJ, Cohen I (2010) Direct measurements of island growth and step-edge barriers in colloidal epitaxy. *Science* 327(5964):445–448.
26. Han Y, et al. (2008) Geometric frustration in buckled colloidal monolayers. *Nature* 456(7224):898–903.
27. Nagamanasa KH, Gokhale S, Ganapathy R, Sood AK (2011) Confined glassy dynamics at grain boundaries in colloidal crystals. *Proc Natl Acad Sci USA* 108(28):11323–11326.
28. Read WT, Shockley W (1950) Dislocation models of crystal grain boundaries. *Phys Rev* 78(3):275–289.
29. Barabasi A-L, Stanley HE (1995) *Fractal Concepts in Surface Growth* (Cambridge Univ Press, New York).
30. Yoon DY, Cho YK (2005) Roughening transitions of grain boundaries in metals and oxides. *J Mater Sci* 40(4):861–870.
31. Lobkovsky AE, Karma A, Mendelev MI, Haataja M, Srolovitz DJ (2004) Grain shape, grain boundary mobility and the Herring relation. *Acta Mater* 52(2):285–292.
32. Hoyt JJ, Asta M, Karma A (2003) Atomistic and continuum modeling of dendritic solidification. *Mater Sci Eng Rep* 41(6):121–163.
33. Trautt ZT, Upmanyu M (2005) Direct two-dimensional calculations of grain boundary stiffness. *Scr Mater* 52(11):1175–1179.
34. Foiles SM, Hoyt JJ (2006) Computation of grain boundary stiffness and mobility from boundary fluctuations. *Acta Mater* 54(12):3351–3357.
35. Nguyen VD, Hu Z, Schall P (2011) Single crystal growth and anisotropic crystal-fluid interfacial free energy in soft colloidal systems. *Phys Rev E Stat Nonlin Soft Matter Phys* 84(1):011607-1–6.
36. Derks D, Aarts DGAL, Bonn D, Lekkerkerker HN, Imhof A (2006) Suppression of thermally excited capillary waves by shear flow. *Phys Rev Lett* 97(3):038301-1–4.
37. Skinner TOE, Aarts DGAL, Dullens RPA (2010) Grain-boundary fluctuations in two-dimensional colloidal crystals. *Phys Rev Lett* 105(16):168301-1–4.
38. Werner A, Schmid F, Muller M, Binder K (1997) Anomalous size-dependence of interfacial profiles between coexisting phases of polymer mixtures in thin-film geometry: A Monte Carlo simulation. *J Chem Phys* 107(19):8175–8188.
39. Haslam AJ, et al. (2003) Stress-enhanced grain growth in a nanocrystalline material by molecular-dynamics simulation. *Acta Mater* 51(7):2097–2112.
40. Zhang H, Srolovitz DJ, Douglas JF, Warren JA (2009) Grain boundaries exhibit the dynamics of glass-forming liquids. *Proc Natl Acad Sci USA* 106(19):7735–7740.
41. Schall P, Cohen I, Weitz DA, Spaepen F (2006) Visualizing dislocation nucleation by indenting colloidal crystals. *Nature* 440(7082):319–323.
42. Pieranski P (1981) *Physics of Defects*, eds Balian R, Kleman M, Poirier JP (North-Holland, Amsterdam), pp 183–200.
43. Cahn JW, Mishin Y, Suzuki A (2006) Coupling grain boundary motion to shear deformation. *Acta Mater* 54(19):4953–4975.
44. Cahn JW, Taylor JE (2004) A unified approach to motion of grain boundaries, relative tangential translation along grain boundaries, and grain rotation. *Acta Mater* 52(16):4887–4898.
45. Trautt ZT, Adland A, Karma A, Mishin Y (2012) Coupled motion of asymmetrical tilt grain boundaries: Molecular dynamics and phase field computer simulations. *Acta Mater* 60(19):6528–6546.
46. Karma A, Trautt ZT, Mishin Y (2012) Relation between equilibrium fluctuations and shear-coupled motion of grain boundaries. *Phys Rev Lett* 109(9):095501-1–5.
47. Zhang H, Srolovitz DJ, Douglas JF, Warren JA (2007) Atomic motion during the migration of general [001] tilt grain boundaries in Ni. *Acta Mater* 55(13):4527–4533.
48. Zhang H, Srolovitz DJ, Douglas JF, Warren JA (2006) Characterization of atomic motion governing grain boundary migration. *Phys Rev B Condens Matter* 74(11):115404-1–10.
49. Sollich P, Lequeux F, Hebraud P, Cates ME (1997) Rheology of soft glassy materials. *Phys Rev Lett* 78(10):2020–2023.
50. Zhang H, Du D, Srolovitz DJ, Mendelev MI (2006) Determination of grain boundary stiffness from molecular dynamics simulation. *Appl Phys Lett* 88(12):121927-1–3.
51. Haxton TK, Liu AJ (2007) Activated dynamics and effective temperature in a steady state sheared glass. *Phys Rev Lett* 99(19):195701-1–4.
52. Crocker JC, Grier DG (1996) Methods of digital video microscopy for colloidal studies. *J Colloid Interface Sci* 179(1):298–310.