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# Entropic stabilization of nanoscale voids in materials under tension

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While preexisting defects are known to act as nucleation sites for plastic deformation in shocked materials, the kinetics of the early stages of plastic yield are still poorly understood. We use atomistic simulation techniques to investigate the kinetics of plastic yield around small preexisting voids in copper single crystals under uniaxial tensile strain. We demonstrate that, at finite temperatures, these voids are stabilized by strong entropic effects that confer them significant lifetimes even when the static mechanical instability limit is exceeded. By virtue of its entropic nature, this effect is shown to be proportionally stronger at higher temperatures. Even accounting for thermal activation, very small voids prove to be extremely inefficient nucleation sites for plasticity.

In contrast to brittle materials, ductile metals usually fail via the nucleation, growth, and coalescence of voids. Because of their pivotal role in failure, the evolution of voids in metals under mechanical loading has been the subject of intense investigation [1, 2]. In spite of this sustained interest, the mechanisms by which nanoscale voids grow have remained somewhat controversial for a long time and many candidate mechanisms have been proposed, including vacancy diffusion [3, 4] and emission of prismatic [5, 6] or shear dislocation [7–11] loops. While the mechanistic aspects are increasingly well understood, largely through atomistic simulation studies, the kinetics associated with plastic yield triggered by preexisting nanoscale voids have only recently begun to be investigated [12]. An understanding of kinetics is essential to assess the relative efficiency of the different nucleation sites and mechanisms of plastic deformation and failure, especially in cases where the mechanical loading is transient, as during shock compression and release.

We take an important step towards this objective by numerically investigating the kinetics of plastic yield at a preexisting nanoscale void in monocrystalline copper under uniaxial tension. We show that strong entropic effects can stabilize voids for significant amounts of time even when the static mechanical instability limit of the system is exceeded. This severely limits the range of strains at which these defects can act as efficient plasticity sources, and hence the likelihood that they dominate the early stages of plastic deformation.

Our study makes use of a wide range of atomistic simulation techniques. The kinetics of plastic yield is directly observed using fully dynamical simulations methods, i.e., molecular dynamics (MD) and Parallel Replica Dynamics,[13] an accelerated molecular dynamics (AMD) method [14]. Vibrational properties are computed using the kernel polynomial method (KPM) [15, 16], while thermodynamic properties are obtained using umbrella sampling [17]. Unless otherwise noted, simulations are carried out in the canonical ensemble and uniaxial tensile strain is applied in the [001] direction; lateral dimensions are fixed from the 300K lattice con-

stant in order to investigate the behavior of the system on a fixed energy landscape. We also present some results where the simulation cells were thermally expanded before applying the strain. Results reported here concern nanoscale voids composed of 13 vacancies (formed by removing an atom and its first neighbor shell). We also investigated voids containing 43 vacancies (constructed by removing an atom and its first two shells of neighbors) and observed the same qualitative behavior. The voids are embedded within a periodic monocrystalline matrix of 15x15x15 face-centered-cubic (fcc) unit cells. We verified that larger cells (30x30x30) exhibit similar behavior.

We begin by directly simulating the uniaxial loading of the void using MD with an externally imposed strain rate  $\dot{\epsilon} = 2 \times 10^7 \text{s}^{-1}$ . Fig. 1 shows the variation of the potential energy during the simulation as a function of the imposed strain. The curves differ by about  $3Nk_B T/2$  from the static baseline because of thermal energy equipartition, and the steadily increasing values reflect the elastic strain energy. Each void is initially stable but plastic yield eventually occurs, as indicated by a sudden drop in potential energy. Consistent with the large applied strains, plastic yield considerably decreases the potential energy (by  $\sim 400 \text{ eV}$ ). A typical plastic yield event is shown in the inset of Fig. 1. Two shear-loop partials are here emitted from the immediate neighborhood void (the spherical cluster on the center left section of the inset). These loops grow outwards on different  $\{111\}$  planes and then interact to form a biplanar shear loop. This loop then continues to grow and propagate away from the void. This process is the same as that reported and analyzed in detail previously [7, 10, 11]. In most cases, plastic deformation proceeds by such a cooperative mechanism that involves multiple loops along different slip planes; however, single loops, or non-interacting multiple loops, are also observed. In the present letter, we focus on the initial yield kinetics; larger simulation cells are required to study the subsequent void growth mechanisms.

Fig. 1 exhibits signatures of anomalous yield kinet-

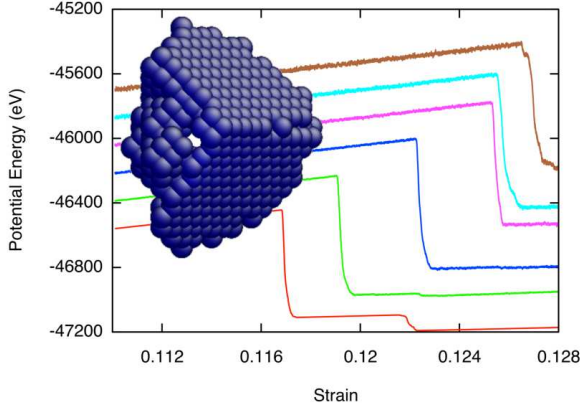


FIG. 1: Potential energy as a function of strain for  $\dot{\epsilon} = 2 \times 10^7 \text{s}^{-1}$ . From bottom to top: Red:  $T=1\text{K}$ ; green:  $T=100\text{K}$ ; blue:  $T=200\text{K}$ ; pink:  $T=300\text{K}$ ; pale blue:  $T=400\text{K}$ ; brown:  $T=500\text{K}$ . Inset: typical plastic yield mechanism at  $\epsilon = 0.12$ . Plastic deformation proceeds by the emission of two partial shear loops on different (111) planes and their eventual merging into a single biplanal loop. Only atoms participating in the deformation are shown.

ics: first, yield occurs *later* at higher temperatures than at lower temperature, and second, voids are dynamically stable up to about 0.01 past the mechanical instability point, i.e., up to about  $\epsilon = 0.126$  (corresponding to a tensile stress  $\sigma_{zz}$  of about 13.5 GPa at 500K), compared to a critical mechanical instability strain of  $\epsilon^* \simeq 0.1162$  (corresponding to  $\sigma_{zz} \simeq 16.5$  GPa at 1K). We observe similar behavior for larger voids (43 vacancies) where the yield point can be delayed by as much as 0.02 past the mechanical instability point (which is around 0.097 in this case). This observation is counterintuitive: in the standard picture of thermal activation, increased thermal energy results in a higher rate of crossing of dynamical bottlenecks, which usually correspond to saddle planes on the potential energy surface. Further, mechanically unstable systems are expected to rapidly fail since no potential energy barrier separates them from lower energy states. In that case, yield would be expected to occur on a vibrational (ps) timescale.

As shown in Fig. 2, the same phenomena are observed in fixed strain MD/AMD simulations at strains beyond the mechanical instability limit. Through the use of AMD methods, we are able to investigate the kinetics down to rates of about  $10^6 \text{s}^{-1}$ , which requires simulation times in the tens of  $\mu\text{s}$ . The yield rates are high at low temperature and decrease extremely fast as the temperature is increased, in agreement with the observed temperature-induced delay of yield. This clearly indicates that the rate-limiting step for yield does not correspond to overcoming a simple potential energy barrier. As expected however, the yield rates increase very rapidly with increasing strain (by roughly two order of

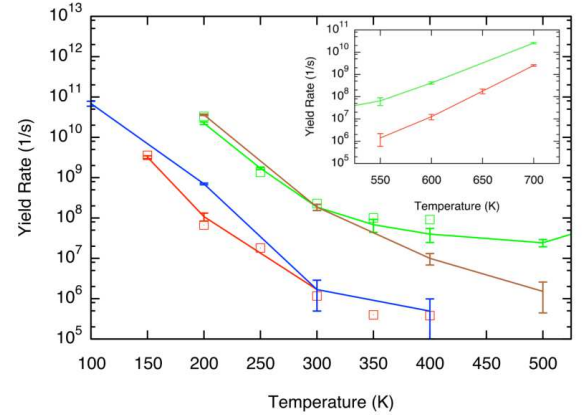


FIG. 2: Yield rate as a function of temperature. Temperature-independent cells: red:  $\epsilon = 0.12$ ; green:  $\epsilon = 0.122$ ; Thermally expanded cells: blue:  $\Delta\epsilon = 0.0025$ ; brown:  $\Delta\epsilon = 0.0045$ . See text for details. Solid line: MD/AMD simulations; symbols: rates predicted from free energy calculations. Inset: high temperature behavior.

magnitude for every 0.2% strain). Fig. 2 also shows that the plastic yield rates turn over as the temperature increases beyond about 500K. Analysis reveals that the yield mechanism is different in this regime: plastic deformation there occurs through homogeneous nucleation of partial dislocation loops [18] away from the void. In this regime, it is interesting to note that the homogeneous nucleation rate has a standard Arrhenius dependence on temperature. We will come back to this point below. It is important to recall that these results were obtained with a fixed cell size, therefore excluding the effect of thermal expansion. When accounting for thermal expansion, the rates no longer decrease with increasing temperature in terms of absolute strains, because of the rapid decrease in the critical strain for mechanical instability. However, as reported in Fig. 2, the strength of the entropic stabilization mechanism strongly increases with temperature in terms of strains  $\Delta\epsilon$  relative to the mechanical instability strain  $\epsilon^*(T)$  (defined as the strain at which unstable phonons appear in the thermally expanded cells). In this case also, an exponential decrease of the yield rate is observed with increasing temperature. These results convincingly demonstrate that a strong stabilization mechanism allows the void to survive intact for extended periods of time despite the apparent mechanical instability of the system.

In order to elucidate the origin of this stabilization effect, we investigate the strain-induced mechanical instability in more detail. We follow the evolution of the system using a steepest descent trajectory starting from an unstable configuration at  $\epsilon = 0.12$  (obtained by scaling a mechanical equilibrium configuration at a sub-critical strain of  $\epsilon = 0.116$ ). Interestingly, this pathway is differ-

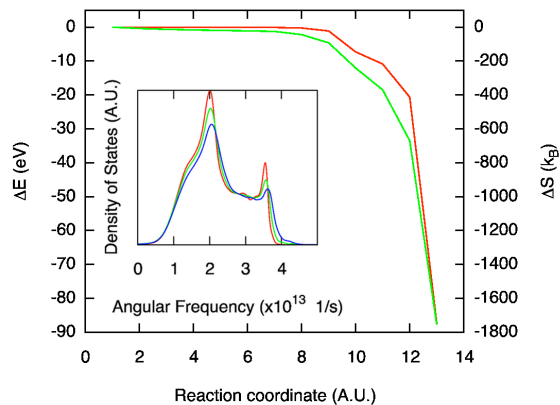


FIG. 3: Energy (red line; left axis) and entropy (green line; right axis) along the minimum energy pathway at  $\epsilon = 0.12$ . Inset: Corresponding vibrational density of states: red:  $r = 1$ ; green:  $r = 12$ ; blue:  $r = 13$ .

ent from what is observed with MD: along the minimum energy pathway (MEP), the void grows through the propagation of a circular crack in a (001) plane. Given the very large strain, a considerable amount of elastic energy is released by cracking, which easily compensates for the cost of the newly created surfaces.

Since the energetics of yield are so favorable, the stabilization process must be of entropic origin. The vibrational density of states (DOS) [as computed through a KPM moment expansion with 500 moments and a stochastic trace evaluation using 500 random vectors [15, 16]] along the MEP is reported in the inset of Fig. 3. The effect of cracking on the vibrational properties of the system is significant: the growth of the crack systematically shifts the vibrational DOS towards higher frequencies. Such a concerted change in a large fraction of the vibrational modes of the system can have a tremendous impact on the free energy landscape of the system. Indeed, the Helmholtz free energy (FE) along the MEP (indexed by a reaction coordinate  $r$ ) can be written as:

$$F(r) = -k_B T \ln Z^*(r) = V(r) - TS(r) \quad (1)$$

where the partition function  $Z^*(r)$  is obtained by integration in the space perpendicular to the MEP. This integral is here carried out in the harmonic approximation using a KPM moment expansion. As the entropy decreases with increasing frequencies, a shift of the DOS towards higher frequencies therefore leads to an increase of the FE. In the present case, this increase is very large: the entropy changes by  $-1766k_B$  from  $r = 1$  to 13 (Fig. 3). This entropic contribution will rapidly cause the appearance of a free energy barrier along the MEP. At  $\epsilon = 0.12$ , the barrier is of the order of 0.14 eV at 100K, rapidly climbing to 0.31 and 0.52 eV at 150 and 200K, respectively. Such barriers will effectively suppress transitions along

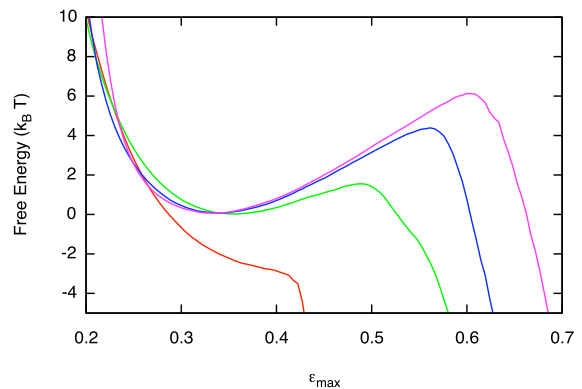


FIG. 4: Evolution of the free energy as a function of maximal relative bond-stretch coordinate with temperature at a strain of  $\epsilon = 0.122$ . From bottom to top: Red:  $T=150\text{K}$ ; green:  $T=200\text{K}$ ; blue:  $T=250\text{K}$ ; pink:  $300\text{K}$ .

the MEP, which explains why this mechanism is not observed at finite temperatures, despite being barrier-less as far as the energetics are concerned.

The entropic stabilization process can be understood in a simple manner. To first order, the change in entropy associated with a change in volume is given by  $\Delta S = \alpha B \Delta V$ , with  $\alpha$  the volumetric thermal expansion coefficient,  $B$  the bulk modulus, and  $\Delta V$  the change in volume [19]. This is a simple consequence of the fact that, due to anharmonicity of the interaction potential, phonons generally become softer with increasing volume, which leads to an increase in vibrational entropy. Conversely, this relation also implies that void growth mechanisms – which effectively decreases the volume vibrationally available to the system – will lead to a decrease of the vibrational entropy. While it might be energetically beneficial for the void to grow, the entropic contribution will create an effective free energy barrier to resist that change. It is important to recall that the processes here occur at fixed total volume; what induces the entropic stabilization is the *change* in free volume *along* the reaction coordinate. For Cu,  $dS \simeq 0.5k_B/\text{\AA}^3$ , which translates into a decrease in entropy of about  $6k_B$  for every atomic volume added to the void.

While the previous analysis focused on the entropic suppression of transitions along the MEP, the argument given above applies to any void growth mechanism. This is consistent with the results of Fig. 2: while cracking is not observed at finite temperatures, the dislocation-mediated mechanism is also strongly suppressed as the temperature is increased, again pointing to an entropic origin. In order to quantify this, we used umbrella sampling [17] to compute free energy profiles along a generic reaction coordinate  $\epsilon_{\max} = \max_i |(r_i - r_{i,\text{ref}})/r_{i,\text{ref}}|$  that measures the maximal relative stretch of any first neigh-

bor bond [20] with respect to a reference state obtained by scaling a slightly sub-critical equilibrium configuration up to the desired strain. While not tuned to any specific mechanism, this coordinate captures the key features that describe the stability of the void and bypasses the difficulty of obtaining a reaction coordinate that constrains all possible variants of the yield mechanism. Results from this procedure are shown in Fig. 4 for  $\epsilon = 0.122$ . At low temperatures ( $< 175\text{K}$ ), the system is unstable and can spontaneously yield; however, as the temperature increases, the large deformations that ultimately lead to yield (corresponding to large values of  $\epsilon_{\text{max}}$ ) are increasingly suppressed by the formation of finite free energy barriers. By the time the temperature reaches  $300\text{K}$ , the barrier to yield is already  $\approx 6k_B T$ . These values are entirely consistent with the rates reported in Fig. 2. Assuming a constant prefactor  $\nu = 10^{11}\text{s}^{-1}$  and a rate of the form  $k = \nu \exp(-\Delta F/k_B T)$ , one obtains rates (hollow symbols) that are in excellent agreement with the MD/AMD results (solid lines). This clearly points to an efficient entropic stabilization mechanism that strongly disfavors any void growth mechanism, and hence enhances the stability of small voids.

Our results indicate that it is extremely unlikely that small nanoscale voids act as efficient nucleation sites for plasticity in shocked metals. While it was already recognized that, because of their small sizes, very large strains and stresses are required to mechanically destabilize these voids [11], our results show that these voids are further stabilized by entropic effects, so that dislocation emission rates remain low for strains away from the (static) mechanical instability limit. In typical shock conditions where the dwell time under tension is typically measured in microseconds, nucleation of plasticity at small void such as these is therefore extremely inefficient. Even for slightly larger voids (43 vacancies), the yield rates becomes significant only at strains of about 0.11, which is within 0.01 of the homogeneous nucleation regime. Because the prefactor for the homogeneous nucleation rate is so large (it is proportional to the number of atoms in non-defective bulk regions), heterogeneous nucleation at these voids will almost certainly not be competitive. In real materials, where many kinds of other defects (grain boundaries, dislocations, inclusions, surfaces, etc.) abound, other sources of plasticity will certainly take over before the homogeneous limit is approached. Note that, because of the very strong dependence of the lifetime of the voids with strain, the same conclusions are very likely applicable to low strain rate, or even static, failure. Indeed, extrapolating from the trend observed here, small voids under strains as high as 0.11 could easily have lifetimes of hours or more. This is also consistent with recent atomistic simulations of voids under shear leading, where they were found to be extremely stable. [12]

This work also serves as a reminder that processes in-

volving large changes in free volume or in strain state between minima and transition states can be expected to have atypical kinetics; as a general rule one would expect unusually slow (fast) rates for processes where the free volume increases (decreases) along the reaction coordinate. For example, Uberuaga *et al.* [21] recently observed that rate of collapse of a void into a stacking fault tetrahedron in Cu — which causes a decrease in the free volume — has a huge vibrational prefactor. Similarly, prefactors of dislocation nucleation rates in nanopillars under compression [22] are reported to be very large [23]. In this context, the compressive strain release would tend to collectively decrease phonon frequencies during dislocation nucleation, leading to the large prefactors. Entropic stabilization of a mechanically unstable system is an extreme case that can be expected to occur for transitions that involve very large increases in free volume. In contrast, we observe that the system is not stabilized against homogeneous nucleation, which is not associated with a large change in the free volume, and that the kinetics for this process remain Arrhenius. This was also observed in Ref. 24, albeit under very large strain rates. In order to correctly predict the kinetics of strained systems it is therefore critical to carefully assess the specifics of each transition mechanism, as assuming standard kinetics could lead to errors of many orders of magnitude in the predicted rates. [18, 25]

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