Continuum nanomechanics for nanocrystalline and ultrafine grain materials

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Abstract. An extension of the classical continuum mechanics model is provided for the solution of boundary value problems at the nanoscale. The resulting continuum nano-mechanical model is based on the introduction of new terms to account for the interaction of bulk and surface points of the medium, which becomes significant as the specimen size is reduced down to the nanometer level. The model can be used to interpret deformation and diffusion phenomena in nanocrystalline (NC) and ultrafine grain (UFG) polycrystals, where a large number of internal surfaces (e.g. grain/twin boundaries) are present. When small material volumes are considered, random effects of the underlying microstructure become pronounced and their interpretation cannot be addressed with deterministic models alone. In this case, the continuum nanomechanics model may be enhanced with stochastic terms accounting for their competition with their deterministic gradient counterparts. The resulting combined gradient-stochastic model can be used to interpret intermittent plasticity and size-dependent serrated stress-strain curves in micro/nano pillars. These ideas have been applied to address certain benchmark problems and configurations of nanoelasticity, nanodiffusion and nanoplasticity. Non-singular expressions can be derived for stresses and strains in the neighborhood of dislocation lines and crack tips contained in a nanograin. Non-linear concentration depth profiles for diffusion in NCs are obtained in agreement with experiments. Corresponding results are obtained herein for coupled elasto-diffusion processes and related size-dependent phase transformation diagrams. When differential equations are not available, deformation features may be revealed through a statistical analysis of the relevant experimental data. This is done here for the interpretation of statistical features of deformed UFG alloys exhibiting serrated stress-strain curves and fractal shear bands.

1. Introduction

The continuum mechanics model (e.g. classical elasticity) has been used to determine the stress and strain distributions in small volumes, such as those around dislocation cores and crack tips. It has also been used to address deformation and fracture of nano-objects such as nano-tubes, nano-beams and grapheme. This model is an alternative to atomistic molecular dynamics simulations which cannot be directly employed for nanoengineering applications and the formulation/solution of related boundary value problems at the nanoscale. For specimens of nanometer size, surface effects become pronounced and bulk-surface interactions should be accounted for. Surface stress elasticity theories assuming different elastic moduli for the bulk and the surrounding surface are available but there are difficulties with the identification of elastic parameters. Moreover, they do not apply when plastic flow occurs. This, in particular, is the case for nanocrystalline (NC) and ultrafine grain (UFG) polycrystals and specimens produced, for
example, with severe plastic deformation (SPD) techniques. A promising possibility for remedying the situation is to generalize the classical continuum mechanics model with a length-scale parameter whose effect becomes more pronounced as its ratio to a characteristic dimension of the specimen increases beyond a certain threshold value which depends on the specimen’s microstructure and size. A rather natural way that such internal length (IL) effects can be accounted for, is by relating the average values characterizing the response of a material volume with the local response. This results to an expression between average and local fields where the Laplacian appears as the leading term. Corresponding gradient nanoelasticity and nanoplasticity models are then generated. The same can be done for diffusion and coupled gradient elasto-diffusion processes governing size-dependent spinodal regions and corresponding size-dependent phase transformation diagrams. When random effects are pronounced and deterministic models are not able to describe related statistical data and obtain power-law exponents, combined gradient-stochastic nanoplasticity models and Tsallis-q entropy statistics may be used to capture the observed behavior.

One of the modest goals of this contribution is to outline a possible extension of the standard continuum mechanics model to describe deformation and diffusion processes in nanocrystalline (NC) and ultrafine grain (UFG) polycrystals [1-20]. The basic premise that this extension builds upon is the explicit recognition of the critical role of the surface – to – volume ratio parameter. This manifests in revising the continuum mechanics model through the introduction of extra terms accounting for the interaction of bulk and surface material points and assuming gradient-dependent constitutive equations for these terms to reflect the aforementioned long-range interaction [15, 18]. This revision is motivated by corresponding experimental observations that reveal the dominant deformation mechanisms at the nanoscale and incorporate them into a continuum description. It is noted, in this connection, that the classical (Euler – Cauchy) model of continuum mechanics has been generalized over the last several decades to describe materials and phenomena at various scales of observation including standard laboratory macroscopic and microscopic scales, geological and oceanic scales, as well as atmospheric and astrophysical scales. Generalized continuum mechanics models for media with microstructure and relativistic continuum mechanics for celestial processes have also been developed. A generalization of the continuum mechanics model, however, has not been used effectively to address nanoscale phenomena for the following reasons: (i) The nanotechnology field is quite new and the needs for extensive structural and manufacturing applications have not been defined yet. (ii) The experimental procedures used at standard macroscopic laboratory scales only now are being extended down to submicroscopic and nanoscopic scales (STM, AFM, micro/nano-indenters and micro/nano-tensile machines, lab-on-a-chip). (iii) The usual trend for modeling nanoscale phenomena is to employ ab initio coupled with molecular dynamics (MD) simulations, as the increasing computer power allows the handling of millions of atoms for realistic
computing times. Nevertheless, for engineering applications and nano-components/nano-devices deformed elastically or plastically in the presence of a thermally or chemically varying environment, an extension of the continuum framework may offer a robust first order solution. An attempt for such extension is summarized here, through the proposed gradient nanomechanics model.

The term “nanomechanics” was introduced by the author [1] in the mid-nineties in two symposia in Osaka and Beijing when he suggested to use continuum mechanics to model deformation and fracture at the nanoscale. This was motivated by ongoing (then pioneering) experimental observations at Michigan Tech (MTU) for the deformation and fracture of NC and UFG polycrystalline specimens in thin film and bulk configurations [2-5]. The experimental observations were concerned with the deformation mechanisms recorded in the TEM during in situ straining of nanopolycrystalline thin films, as well as with the tension/compression response of ultrafine grain bulk specimens. It was then suggested [4, 6-7] to account for these observations through the introduction of higher order gradients of constitutive variables in the standard equations of elasticity and plasticity. This allowed to interpret non-standard effects associated with the heterogeneities and incompatibilities developed in the neighborhood of grain boundary space which, in contrast to conventional polycrystals, should be treaded on equal footing as the grain interior space in the case of NC and UFG materials. Related composite (two-phase) models (assigning different properties to the grain boundary and grain interior “phases”) for NCs and UFGs have been proposed within the aforementioned initial attempts of the MTU group to interpret the inverse Hall-Petch equation [8]. These were refined subsequently [9-12] and further documented in agreement with experiments. Such type of models have been used extensively by many researchers in this field [13, 14], sometimes without proper reference or credit to the original idea. An alternative (to the mixture model) is to generalize the balance laws for an elementary volume with an extra nonlocal (long-range) term accounting for the effect of surrounding surface on the material point under consideration. This has been discussed by the author in [15] and this discussion is expanded somewhat here to consider nanodiffusion and propose evolution equations for dislocations and related structural defects in NC and UFG materials. In this sense, the present article may be considered as a follow-up of [15].

In a “bulk-surface interaction” continuum model the geometric nanoscopic irregularities occurring either at internal or external surfaces (for example, in the form of “facets” or “steps” respectively) are “smoothed” out, and this is the reason for introducing the aforementioned extra penalty terms [16] in the standard balance laws of continuum mechanics, for which gradient type constitutive equations are assumed. The generalized balance equations with source/sink (interaction) terms can be formally reduced to the standard balance equations of continuum mechanics by redefining stress and flux at a point for an elementary material nanovolume. The
corresponding gradient constitutive equations take into account phenomenologically the geometric configuration of the nanostructural defects and their interactions. The existing nanoirregularities at internal and external surfaces are also taken into account in a phenomenological way through appropriate (based on corresponding experimental observations) boundary conditions. This point of view is motivated by a 1978 proposal of the author for a continuum with microstructure [17], sketched in an effort to model self-diffusion in solids. The exchange terms of effective “mass” and “momentum” between bulk and surface points in this case were the vacancies, and the resulting surface irregularities by their internal motion was “smoothed out” by appropriate effective boundary conditions for their concentration and flux. In the case of plasticity, the carriers of effective “mass” and “momentum” are the dislocations and related structural defects. Both the “mixture” and the “bulk-surface interaction” approaches were reviewed by the author in [18].

The plan of the paper is as follows: Section 2 summarizes the pioneering experimental findings of nanoplasticity mechanisms for NC thin films and UFG bulk nanopolycrystals. Section 3 summarizes simple deterministic nanoelasticity, nanodiffusion, nanoplasticity and multi-element nanodefect kinetics models. These models can be enhanced with stochastic terms to account for random micro/nanostructures. The resulting combined gradient-stochastic models have been used recently to address size-dependent serrated flow in micro/nano pillars. However, this effort is still in progress, some preliminary results have been reported in [19], and a more detailed account will be provided in a forthcoming article. Section 4 summarizes some recent nanoscale results which cannot be obtained with existing models. It considers, moreover, two benchmark problems of substantial current interest. The first problem is concerned with size-dependent spinodal regions/phase diagrams, and a gradient coupled elasto-diffusion model for NC materials is used to interpret the experimental trends. The second benchmark problem is concerned with intermittend/serrated plastic flow and multiple fractal shear bands observed in UFG alloys. No model equations are available to interpret the experimental findings in this case. Also, the data cannot be interpreted by standard statistics and related power laws based on classical Boltzmann-Gibbs-Shannon thermodynamics. Instead, Tsallis q-entropy (non-extensive) thermodynamics are used with reasonable success.

2. Summary of the Main MTU Experimental Observations

This section summarizes the pioneering experimental observations of the MTU group which have motivated the proposed continuum nanomechanics models for NC and UFG materials. We insist upon briefly reviewing these results here (a more detailed account can be found in [6], and in a selective review on mechanisms and models for nanocrystals [20]), as they have been largely overlooked by current workers in the field. In particular, the first two figures
shown in this section were the first micrographs obtained for NC thin films (showing nano-pore nucleation by local mass diffusion in the absence of dislocation activity) and for UFG alloys (showing “massive” multiple shear banding as the sole mechanism of plastic slow resulting to a perfect, as opposed to strain hardening plasticity behavior). Similar micrographs elucidating the nature of plastic deformation for nanoscale configurations have appeared in the sequel for multiple shear banding in [21,22] and for nano-pore nucleation – induced nanocrack growth in [23]. [Apparently, the authors of this last article by Wei Yang’s group in China and their collaborators in US were not aware of the previous work of the MTU group].

2.1 Deformation Mechanisms in NC Thin Films [2,3]: In a typical experiment, a crack is nucleated near a hollow TEM specimen; i.e. a ~3mm disk with a small hole prepared by ion machining. The crack develops through the film thickness and the plastic deformation behavior is observed near the crack faces and ahead of the crack tip. This was accomplished by videotaping the in situ straining experiments, and also by taking high-resolution photographs at various stage of deformation. It is noted, in particular, that the metal nanograins can be imaged in a “lattice resolution” mode; i.e. some actual crystal planes in each grain are imaged by the microscope. This allows keeping track of grain displacement and rotation since the angles between adjacent grains can be easily measured before and after straining.

The latter was confirmed through lattice and atomic-resolution imaging with an image intensifier revealing that the deformed gold (8 nm diameter) nano-grains were virtually dislocation free. This lack of dislocations, in conjunction with the observation of rapid nano-pore growth, suggests that grain boundary sliding may be the dominant plasticity mechanism, even though the homologous temperature is very low. Such diffusion induced plastic deformation mechanisms at low homologous temperatures are not observable in conventional polycrystals where plasticity is dominated by dislocation activity.
A direct manifestation of mass diffusion induced plasticity (instead as dislocation motion) as depicted in Fig. 1, showing the nucleation of a nanovoid in a triple grain boundary junction. The initially nucleating nano-pore grows under the action of high local stress triaxiality present at the tip of a crack, occurring under the beam possibly due to “thermal” stresses or “clamping” stresses from the holder. As the nano-pore coarsens by mass diffusion upon further straining under the electron beam, the crack grows through the grain boundaries and a ligament is formed (indicated by an arrow) connecting two different grains. This, in turn, is also eliminated by mass diffusion leading to further crack advance and crack tip blunting.

A general conclusion that can be drawn from the above described MTU \textit{in situ} deformation nanopolycrystalline thin film tests is that extensive plasticity occurs in the absence of dislocation activity within individual grains. That is, no dislocation images were observed within the grains after straining, and no contrast changes associated with moving dislocations were observed on the videotape during \textit{in situ} straining. This indicates that plasticity was due to grain boundary processes leading to grain sliding and rotation, as well as nano-pore nucleation and growth at more advanced stages of straining. The lack of experimentally observed dislocation activity certainly suggests that the local stress never exceeded the yield limit of individual grains. Independent but analogous \textit{in situ} straining tests conducted on silver thin films with grain sizes around 110 nm, exhibited traditional dislocation-based plasticity. At a 10 nm grain sizes, where
no apparent dislocation activity was observed, fracture was intergranular, while at an 110nm grain size where significant dislocation activity occurred, fracture was transgranular. Further work needs to be done in order to experimentally identify the transition grain size. The observation of dislocation activity in the larger-grained films is important, because it verifies that there is no experimental difficulty in imaging dislocations in these nanostructured thin film-straining experiments when dislocations are present. It may be argued that nano-grained metals deform by very rapid dislocation activity, in which dislocations sweep from grain boundary to grain boundary almost instantaneously, thus precluding direct observation. While this may or may not be the case in bulk nanostructured metals, it is difficult to imagine that such a mechanism could occur in thin films like the ones studied here without significant and experimentally measurable consequences. In this connection, it may be argued that one such “measurable consequence” of dislocation activity with a nanograin is texture evolution. [Certain recent reports and conference discussions seem to support this argument for NC materials and this issue will be discussed in the future.]

2.2 Deformation Mechanisms in UFG Bulk Nano-polycrystals [5]: The production of bulk nanostructures for load-bearing components has been problematic for the entire materials community as this is only possible in processes occurring far from equilibrium by techniques such as gas condensation, ball milling, or thin film deposition. The product is a powder or thin film that must be consolidated. Consolidation of powders generally requires time at high temperatures, which coarsens the grain size catastrophically. Two procedures have been utilized by the MTU group to avoid catastrophic coarsening during consolidation. First, a two-component system (Fe/Cu) which phase-separates has been chosen for initial studies; this type of system allows for pinning of grain boundaries by the minor phase, resulting in less coarsening. Second, rapid powder forging techniques have been adopted to fully consolidate nanostructured powders in a very short time at high temperature. Mechanical ball milling was used to produce nanostructured powder particles with grain sizes around 15 nm (grain sizes down to 4nm have been achieved by others with this method). A 90% Fe - 10% Cu alloy was studied, because copper is insoluble in iron. The structure which results after consolidation consists of copper precipitates on the iron grain boundaries, and these precipitates impede grain growth during processing. Consolidation of the powders into bulk materials was accomplished by hot isostatic pressing (HIP) and forging. The HIP technique was not able to consolidate Fe/Cu materials to full density without coarsening the grain size to a minimum of 100nm. As the absence of shearing mode in the isostatic press precludes the shear flow necessary to heal processing defects, rapid powder forging offers an alternative consolidation procedure that resulted in fully-dense bulk nano-polycrystalline specimens with very high purity.
In such a composite, it is reasonable to postulate that the amorphous phase might control the mechanical behavior, and this would result in similarities between amorphous and nanostructured metals. However, in this study, amorphous-like behavior (multiple shear banding deformation mechanism) was observed at grain sizes up to almost 2 µm; in this size regime, the fraction of boundary material is negligible, so amorphous-like behavior would be difficult to rationalize based on such type of composite model. An alternative view leading to another type of a two-phase deformation induced model may be expressed as follows: in the larger grain size alloys, homogeneous dislocation motion takes place inside the grains but localized instabilities take place in the neighborhood of the highly non-equilibrium grain boundaries where dislocations interact with the small Cu precipitates leading to locally discontinuous grain sliding and rotation. These deformation inhomogeneity induced instabilities manifest themselves at meso and macro scales with the formation and evolution of a massive shear band structure, with surface effects being now generated through interactions between the “bulk” and the “shear band” region. In the interconnected shear band region an intense plastic deformation occurs, whereas in the underformed between the shear bands region (which supports the occurrence of such localized deformation) plastic flow is relatively constrained. The occurrence of this massive multiple shear banding plasticity mechanism is depicted in Fig. 2, for various grain size UFG compressed specimens. An interesting point is that the grain sizes present in these nanostructured alloys are on the same order of magnitude as the sub-grain size which is typically obtained before cold-worked metals begin to undergo shear-banding instabilities. This similarity may be a key in understanding shear banding, both in nanostructured metals and heavily cold worked metals.

Fig. 2: Optical micrographs showing deformation and fracture behavior under compression of nanostructured Fe-10% Cu alloy for different grain sizes. Shear fracture occurred rapidly at the finest grain sizes. Shear bands and shear offsets occur at coarser grain sizes. Buckling, instead of fracture, is noted at a larger grain size. Wavy lines are intersections of shear bands coming out of the plane of the paper at an angle. Note the increase in width of shear bands at increasing grain sizes. The compression axis was vertical.
The mechanism of plastic deformation inside the shear bands is a topic of continuing study. Transmission electron microscopy of shear-banded material has revealed that the deformation within the bands is intense, while there is no deformation outside the bands. Fig. 3 shows transmission electron microscope photos of a nanostructured iron alloy HIP’ed at 600°C, with an average grain size around 100 nm. In Fig. 3a the grains maintain their original structure, while in Fig.3b the grains have been deformed and elongated to an aspect ratio of about 10:1. These photos were taken in adjacent regions of the same specimen, approximately 10 µm apart, giving a lucid evidence of the localized deformation mechanism that takes place.

![Fig. 3: TEM micrographs of a compression-tested sample with a 100-nm grain size, showing highly localized deformation. Both photos are from the same foil, in areas separated by about 10 µm. (a) Undeformed area outside the shear band region, identical to as HIP material; and (b) heavily deformed area in the shear band region. Elongated grains are noted, as a result of grain boundary processes (sliding and rotation) most likely caused by both intra and inter grain boundary dislocation activity.](image)

It follows from the above observations of the MTU group [6], that the behavior of the UFG and nanopolycrystalline Fe-Cu% materials is unique. They act like metallic glasses and amorphous polymers with respect to deformation localization, shear band angles, and the tension-compression anisotropy of strength but they behave like steels with respect to Hall-Petch behavior (and also temperature sensitivity of strength as documented elsewhere). These observations offer the opportunity to fully explore deformation instabilities in several classes of materials, in general, across the length scale spectrum spanning from the subnanometer (amorphous) and nanometer (nanopolycrystals) to submicrometer/micrometer (ultrafine and fine-grained) and millimeter/centimeter traditional materials. In particular, for the nanometer NC and submicrometer UFG metals discussed here we present in the next section gradient
nanomechanics models to address their deformation and diffusion behavior. Such type of deformation behavior has also been subsequently observed in other classes of novel materials including bulk NC and UFG materials produced by severe plastic deformation (SPD) techniques [24,25]. In this latter class of materials it has been observed that a bi-modal grain size distribution allows for the possibility to optimize mechanical properties by adjusting the ductility-to-strength ratio. As already mentioned, the phenomenon of multiple or “massive” shear banding accompanied by a concurrent almost perfectly plastic behavior (as reflected in the experimental stress-strain graph), has also been more carefully analyzed for NC iron in [21]. The “smaller” size grains here may play the role of the small Cu precipitates in the case of the Fe-10%Cu alloys.

3. Gradient Nanomechanics

An extended continuum mechanics framework is outlined here for addressing the mechanical response of NC and UFG polycrystals. This extension is based on generalizing the standard continuum mechanics structure by introducing extra terms modeling the interaction between “bulk” and external or internal “surface” points, as well as appropriate constitutive equations for these terms.

3.1 Nanoelasticity: Within this approach the standard equilibrium equation $\text{div } \sigma = 0$ is generalized to include an additional internal body force $\hat{f}$ representing the exchange of momentum between bulk and surface for the present case of small volumes. Then, the balance law of linear momentum in the absence of inertia effects reads

$$\text{div } \sigma^B = \hat{f},$$

(3.1)

or in indicial notation $\sigma_{ij,k} = \hat{f}_{i,j}$, where $\sigma^B$ is the usual stress tensor of the bulk material and $\hat{f}$ is an internal-like force modeling the momentum exchange between the “bulk” and “surface” points. It is further assumed that $\hat{f}$ is determined by a higher-order stress or “hyperstress” $\mathcal{M}$ of third order which, in turn, may be expressed as the gradient of the second-order stress $S$ or extra stress modeling bulk-surface interaction. It follows that

$$\hat{f} = \text{div } \text{div } \mathcal{M} ; \quad \mathcal{M} = \nabla S,$$

(3.2)

or in indicial notation $\hat{f}_i = \mathcal{M}_{j,k,j} ; \quad \mathcal{M}_{jk,j,k} = S_{i,j,k}$, where the index summation convention is adopted. The simplest possible constitutive assumption for the extra stress $S$ is to assume it proportional to the bulk stress $\sigma^B$, i.e.

$$S = c \sigma^B,$$

(3.3)

and then Eq. (3.1) can be written as

$$\text{div } \sigma = 0 ; \quad \sigma = \sigma^B - c\nabla^2 \sigma^B.$$

(3.4)
If for $\sigma^B$ we adopt the usual Hooke’s law of classical elasticity, i.e. $\sigma^B = \lambda (\text{tr} \varepsilon) I + 2\mu \varepsilon$, where $(\lambda, \mu)$ denote the Lamé constants, it follows that the total stress $\sigma$, including both the usual stress corresponding to the bulk and its interaction with the surface, is determined by the equation

$$\text{div} \sigma = 0; \quad \sigma = \lambda (\text{tr} \varepsilon) I + 2G \varepsilon - c \nabla^2 \left[ \lambda (\text{tr} \varepsilon) I + 2\mu \varepsilon \right],$$

which are alternatively known as the equations of gradient elasticity. It is noted that the overall stress $\sigma$ is divergence free, i.e. it satisfies the usual equilibrium equations (3.5), but the bulk stress $\sigma^B$ is not divergence free; satisfying a non-standard equilibrium equation $\text{div} \sigma^B = \text{div} \left( c \nabla^2 \sigma^B \right)$. Only when $\sigma^B$ is harmonic, it is also divergence-free i.e. self-equilibrated, satisfying the classical equilibrium equation of the classical Cauchy stress. In this connection, it should be emphasized that the non-singular stress derived for dislocation lines and crack tips (e.g. [26-31]) is not self-equilibrated but it becomes so by taking into account the interaction of bulk with its surrounding surface. A similar remark holds if a displacement field $u$ is introduced in the usual way, i.e. $\varepsilon = 1 / 2 (\nabla u + (\nabla u)^T)$ (i.e. the strain field $\varepsilon$ is assumed to be compatible). The governing equations for $u$ are given by the gradient modification of the Lamé equations which can be written as $\mu \nabla^2 u + (\lambda + \mu) \text{grad div} u - c \nabla^2 \left[ \mu \nabla^2 u + (\lambda + \mu) \text{grad div} u \right] = 0$. Then, if the conditions for the validity of Ru-Aifantis theorem hold (e.g. [29] and references quoted therein), it can be shown that $u$ satisfies an inhomogeneous Helmholtz equation of the form $u - c \nabla^2 u = u_0$ where $u_0$ is a displacement field obtained from the solution of a corresponding classical elasticity solution for the same configuration and same traction boundary conditions. Formal differentiation of this equation gives $\varepsilon - c \nabla^2 \varepsilon = \varepsilon_0$, and non-singular solutions for the strain field $\varepsilon$ can be obtained from this equation for dislocations and cracks under appropriate boundary conditions when the classical-like field $\varepsilon_0$ is assumed to be known.

### 3.2 Nanodiffusion

The approach adopted earlier for a deforming NC or UFG material, viewed as a continuum which interacts with its surface, can be applied to model diffusion processes. It has been experimentally observed that the diffusivity in such materials may be more than ten orders of magnitude higher in comparison to regular lattice diffusion. Grain Boundaries and especially triple grain boundary junctions act as high-diffusivity paths. In fact, diffusion in the bulk crystalline space may be neglected as compared to the diffusion in the intercrystalline IC space (characterized by a diffusivity comparable to grain boundary diffusivity of conventional polycrystals) and the triple junction TJ space (characterized by a diffusivity comparable to conventional surface diffusion). This view may be supported by the fact that the values of
activation energies for diffusion in NC (and UFG) materials are more comparable to surface diffusivities rather than to grain boundary diffusivities in conventional polycrystals [32-34]. For example, at room temperature the activation energies for diffusion of Cu and Ag in n-Cu are 0.64 and 0.36 eV/atom; i.e. similar to the corresponding activation energies for surface diffusion which are 0.69 and 0.3 eV/atom respectively.

Within our proposed bulk-surface interaction approach, the classical Fick’s law for diffusion is replaced by

\[
j = j^B + \hat{j} ; \quad j^B = -D \nabla \rho \quad \text{(3.6)}
\]

where \(D\) is the diffusivity of the bulk material, \(\rho\) is the concentration, \(j^B\) the usual Fickean flux and \(\hat{j}\) an extra flux term to account for the flux exchange between “bulk” and “surface” points. In analogy to previous section for nanoelasticity, it is assumed that \(\hat{j}\) is determined by a second order tensor flux or “hyperflux” term \(J\) such that

\[
\hat{j} = \text{div} J \quad \text{(3.7)}
\]

In the case of steady states \(\left(\partial_t j^B = 0\right)\) the hyperflux \(J\) may be assumed to be proportional to the gradient of \(j^B\) (in analogy to the case of elasticity), while for transient states \(\left(\partial_t j^B \neq 0\right)\) the gradient of \(\partial_t j^B\) should also be taken into account. Thus, the simplest possible constitutive expression for \(J\) is the following form

\[
J = \nabla \left( c j^B + c^* \partial_t j^B \right) \quad \text{(3.8)}
\]

which, upon insertion to Eq.(3.8) and subsequent use of Eq.(3.6), gives

\[
j = -D \nabla^2 \left( c \nabla \rho + c^* \nabla \dot{\rho} \right) \quad \text{(3.9)}
\]

where the classical Fickean expression of Eq. (3.6)$_2$ for \(j^B\) has also been utilized. Upon substitution of Eq. (3.9) into the standard differential statement expressing conservation of mass (the density \(\rho\) is treated as an average quantity for the material volume under consideration), i.e.

\[
\dot{\rho} + \text{div}j = 0 \quad \text{(3.10)}
\]

one obtains

\[
\dot{\rho} = D \nabla^2 \rho + c^* D \nabla^3 \dot{\rho} + c D \nabla^4 \rho \quad \text{(3.11)}
\]

i.e. a higher order diffusion equation containing third and fourth order gradients of the concentration \(\rho\), in addition to the classical diffusion equation. The new phenomenological coefficients or internal length parameters \(c\) and \(c^*\) depend on the nanoscopic configuration (grain size or thickness of grain boundary and the geometric characteristics of triple grain boundary junctions).
3.3 Nanoplasticity: To derive modified equations for plasticity along similar lines, as for the elastic and diffusion cases, we will consider the situation of simple shear. In this case the “equivalent” or “effective” shear stress which is used as the basic quantity for deriving constitutive plasticity equations in three dimensions. Thus, for simple shear conditions (valid along a representative slip plane) we have
\[ \partial_x \tau^B = \hat{f}, \] (3.12)
where \( \tau^B \) is the bulk shear stress in a direction perpendicular to \( x \)-coordinate and \( \hat{f} \) is the one-dimensional scalar counterpart of the exchange of momentum force between “bulk” and “surface” points. As in the elastic case, it is assumed that the scalar \( \hat{f} \) is given by the spatial derivative of another scalar field \( \mathcal{M} \) which, in turn, is given by the spatial derivative of another scalar field \( S \), i.e.
\[ \hat{f} = \partial_x \partial_x \mathcal{M}; \quad \mathcal{M} = \partial_x S. \] (3.13)
Unlike to the elastic case where the interaction of “bulk” and “surface” points can be expressed equivalently either in terms of stress or in terms of strain, in the case of plasticity it is more convenient to assume that the shear strain \( \gamma \) (generated by dislocation motion) determines the bulk-surface interaction. In other words, it is assumed that
\[ S = c \gamma, \] (3.14)
and thus, in view of Eq. (3.13), Eq. (3.12) can be written as
\[ \partial_x \tau = 0; \quad \tau = \kappa \gamma - c\partial_x \gamma, \] (3.15)
where the standard plasticity relation \( \tau^B = \kappa(\gamma) \) was assumed for the bulk stress, and the relation \( \tau = \tau^B - \partial_x \mu \) was assumed for the total (or in this case applied resolved shear) stress \( \tau \). The three-dimensional generalization of Eq. (3.15) reads
\[ \text{div} \sigma = 0; \quad \tau = \kappa(\gamma) - c \nabla^2 \gamma \] (3.16)
where \( \sigma \) is the total stress, \( \tau \) is the equivalent or effective stress \( \tau = \sqrt{1/2 \sigma'_{ij} \sigma'_{ij}}; \quad \sigma'_{ij} = \sigma_{ij} - 1/3 \sigma_{kk} \delta_{ij} \) and \( \gamma \) the corresponding equivalent or effective shear strain.

An alternative way to reach Eq.(3.16) is through homogenization of a microscopic yield condition [35] of the form \( \tau = T^L \cdot \mathbf{M} = \kappa(\gamma) \) where \( T^L \) is the lattice stress (similar to the bulk stress \( \sigma^B \) of the elastic case) and \( \mathbf{M} = 1/2(\mathbf{n} \otimes \mathbf{v} + \mathbf{v} \otimes \mathbf{n}) \) denotes the orientation tensor of a representative slip system \( (\mathbf{n}, \mathbf{v}) \). This was derived by neglecting possible non-uniformities in the momentum balance for the dislocated state of the form \( \text{div} T^D = \hat{f} \), where \( T^D \) is the dislocation stress or internal stress due to individual dislocation interactions and \( \hat{f} \) an internal force modeling the exchange of momentum between dislocations and lattice. [ \( T^L \) is the lattice stress, \( \mathbf{M} \) \]
is the usual symmetric orientation tensor defined by the unit vectors \( \mathbf{n} \) (normal to the slip plane) and \( \mathbf{v} \) (in the slip direction) and \( \gamma \) is the plastic strain in single slip which, after homogenization, is identified with the equivalent plastic strain.\] This assumption of \( \text{div}\mathbf{T}^{D} = 0 \) allows for the microscopic yield condition to be interpreted on the basis of the equation \( \hat{\mathbf{f}} \cdot \mathbf{v} = 0 \) leading to the form \( \tau = \mathbf{M} = \kappa(\gamma) \) when viscoplastic effects are neglected. In the case that inhomogeneous effects (due to climb, obstacles, and other non-slip processes) individual dislocation interactions in the dislocation ensemble cannot be neglected. Then, the dislocation stress \( \mathbf{T}^{D} \) may be written as \( \mathbf{T}^{D} = \mathbf{T}^{inh} + \alpha \) where \( \alpha \) is the usual back stress, and \( \mathbf{T}^{inh} \) is an additional inhomogeneous term to be deduced from a statistical mechanics treatment of the dislocation ensemble. While rigorous 3D statistical mechanics treatments of line defects may be formidable to apply for deducing a rigorous expression for \( \mathbf{T}^{inh} \), a simpler point of view may be taken that such non-uniformities arise from the excess of dislocation density or density of geometrically necessary dislocations \( \rho_{GND} = \rho^{+} - \rho^{-} \). This extra contribution may be represented within the structure of the assumed single slip representative system through the extra constitutive term \( \mathbf{T}^{inh} = \hat{\mathbf{g}}(\mathbf{n}, \mathbf{v}, \nabla \gamma) \), where the usual relation between \( \rho_{GND} \) and the plastic gradient \( \nabla \gamma \) has been used. In view of the random statistical distribution of \( \rho_{GND} \), we first assume that \( \hat{\mathbf{g}} \) is an isotropic function of its arguments. The resulting inhomogeneous part of the dislocation stress contains the tensors \( (\mathbf{n} \otimes \nabla \gamma + \nabla \gamma \otimes \mathbf{n}) \) and \( (\mathbf{v} \otimes \nabla \gamma + \nabla \gamma \otimes \mathbf{v}) \) multiplied by scalars which we assume to be constants for simplicity. By taking the divergence of \( \mathbf{T}^{inh} \), we deduce the inhomogeneous contribution to the microscopic momentum balance for the dislocation state associated with the representative slip system, in the form \( (\mathbf{n} + \mathbf{v}) \otimes \nabla^{2} \gamma + (\text{grad}^{2} \gamma)(\mathbf{n} + \mathbf{v}) \), where \( \text{grad}^{2} \gamma \) denotes the second spatial gradient of \( \gamma \). Next, we take the inner product of the aforementioned expression with the unit vector \( \mathbf{v} \) in the slip direction to deduce the inhomogeneous contribution to the microscopic yield condition. The result is \( \nabla^{2} \gamma + \gamma_{ij}(\mathbf{v}_{i} \mathbf{v}_{j} + \mathbf{v}_{i} \mathbf{n}_{j}) \) multiplied by a scalar coefficient. To obtain the macroscopic counterpart of the inhomogeneous contribution to the yield condition we should integrate over all possible orientations of the slip system \( (\mathbf{n}, \mathbf{v}) \). In doing so we find the contribution of the second term in the above expression to be proportional to \( \gamma_{ij} \delta_{ij} \), i.e., the overall inhomogeneous contribution to the yield condition is proportional to \( \nabla^{2} \gamma \). If the coefficient of proportionality is designated by \( c \), it follows that the macroscopic counterpart of the aforementioned yield condition reads \( \tau = \kappa(\gamma) - c \nabla^{2} \gamma \), which is Eq. (3.16).
We conclude this section by briefly illustrating how internal stress fluctuations can be accounted for. One intuitive way to do this is to generalize Eq. (3.15) to include a stochastic part; e.g. of the form: 

\[ \tau = \kappa |\gamma| + \alpha \frac{\partial^2 \gamma}{\partial \xi^2}; \alpha \rho (\gamma, x) = \alpha h(\gamma) g(x) \] 

In this expression, the new term and \( \alpha \) denotes the fluctuating stress (with \( \alpha \) being a very small number). The quantity \( h(\gamma) \) denotes a deterministic hardening part, \( g(x) \) is a correlation function in space and \( \xi \) denotes the respective correlation length. This has been implemented in a cellular automaton grid to simulate multiple shear banding and corresponding stress-strain graphs for the specimens shown in Fig. 2. The homogeneous stress was assumed to have the form \( \kappa(\gamma) = \gamma + \theta \gamma \), with \( \theta \) denoting the coefficient of linear hardening. Preliminary results have been reported in [15], and more conclusive results will be provided in a future article.

3.4 Nanodefect Kinetics: In the case that the aforementioned nanoplasticity model needs to take explicitly into account the motion and interaction of plastic deformation carriers, it should be supplemented by corresponding evolution equations for the underlying defect state. A first attempt to describe cooperative defect phenomena and dislocation patterning was proposed by Walgraef and Aifantis (W-A model) focusing on the formation and stability of persistent slip bands (PSBs) and the wavelength of the layered dislocation structure routinely observed during cyclic deformation [36]. The W-A model is a system of reaction-diffusion type of equations for the densities of two dislocation populations: the density of immobile dislocations and the density of mobile dislocations. This approach was taken up later by Romanov and Aifantis [37] to discuss cooperative phenomena and interaction of defects (dislocations, disclinations etc.) during monotonic deformation, within a multi-element defect kinetics framework. This framework is further explored below for deforming nanopolycrystals and more definite results will be reported in a future publication. In such NC and UFG materials, the high internal strains developed during processing result into the formation of large populations of defects (dislocations, disclinations, twins etc.) some of which may not play such a significant role in the deformation of conventional polycrystals, as in the case of nanopolycrystals.

The starting point in the multi-element defect kinetics approach is the subdivision of structural defects into different types or populations according to their geometry, mobility and other properties (e.g. long-range elastic fields). Each population is characterized by the partial defect density \( \rho_i \), which evolves in space and time in accordance with the following equations:

\[ \frac{\partial \rho_i}{\partial t} = I(\rho_1, \rho_2) + D_i \nabla^2 \rho_i; \quad i, j = 1, 2, ..., N. \]
The “collision integral” or “source” quantities \( I(\rho, \rho') \) include, in general, non-linear terms which describe the processes of defect generation, multiplication and annihilation, as well as reactions between defects of different type. The Laplacian terms describe the diffusion-like redistribution of defects during plastic deformation. It is noted that Eq. (3.17) includes only diffusion-like gradient terms (with diffusivities \( D_i \)), without the explicit appearance of a divergence “transport-type” term. This is especially relevant for scalar defect densities, since defects and anti-defects (defects of opposite sign) move in opposite directions with the aid of a hopping mechanism, thus resulting in an effective diffusion-like motion, with the diffusivity related directly to the mean free defect path \([36,37]\). The determination of the collision integral terms may be possible by considering the relevant reactions between defects and their cross-sections on microscopic grounds. It is also noted that the existence of defect families with different mobilities allows for the approximation of adiabatic elimination of the fast variables to be used and simplify the solution and stability analysis of relevant diffusion-reaction system \([38, 39]\).

In the presently considered case of nc deforming polycrystals, gliding intergrain and grain boundary dislocations may be considered as mobile defects, while triple-line disclinations and four-fold node point disclinations can be viewed as immobile defects which, however, can react with mobile ones. Additional populations of defects accommodating the plastic incompatibility in junctions and nodes may also be introduced. These populations could include point defects, mobile (but unstable) lattice dislocations, low-mobility dislocation dipoles, disclination dipoles, nanotwins etc. [The main difficulty in the proposed approach is related to the efficient and correct determination of the collision integrals in the reaction-diffusion equations; discrete nanoscopic considerations and molecular dynamics simulations may provide the needed input in this direction]. To proceed further it is assumed that the nc polycrystal is made up by misoriented grains with a typical size \( d \) which are separated by grain boundaries; the typical length of a grain boundary facet also being \( d \). The following populations of defects are distinguished and are characterized by their densities:

- \( \rho \) - mobile dislocations: they are nucleated and move in the grain interior;
- \( \varphi \) – low mobility or immobile dislocations in the form of dislocation dipoles: they also evolve in the grain interior;
- \( \psi \) - grain boundary sliding (mobile) dislocations: they have their Burgers vector parallel to the grain boundary plane;
- \( \theta \) - junction disclinations: they originate from grain boundary dislocations with their Burgers vector normal to the grain boundary plane. Each grain boundary facet may have only two disclinations at its ends. The strength of disclinations relates to the change of the average misorientation at grain boundaries and is designated by \( \omega \).
No distinction is made between defects of opposite sign and existing peculiarities of crystallography are neglected. Then on the basis of appropriate physical considerations concerning the various possible defect mechanisms taking place during deformation, the following system of reaction-diffusion equations may be proposed for the aforementioned defect densities $\rho$, $\varphi$, $\psi$, $\theta$:

\[
\begin{align*}
\frac{\partial \rho}{\partial t} &= A_\rho \rho - B_\rho \rho^2 - C_\rho \frac{\rho}{d} + C_\beta \rho \varphi + \omega \rho \theta + N \frac{\psi}{d} + D_\rho \nabla^2 \rho, \\
\frac{\partial \varphi}{\partial t} &= A_\varphi \rho + B_\varphi \rho^2 - C_\varphi \rho \rho \varphi - K \rho + D_\varphi \nabla^2 \varphi, \\
\frac{\partial \psi}{\partial t} &= C_\psi \frac{\rho}{d} + A_\psi \rho - B_\psi \rho \psi + D_\psi \nabla^2 \psi, \\
\frac{\partial \theta}{\partial t} &= C_\theta \frac{\rho}{d} + A_\theta \rho - B_\theta \rho \theta - G \theta + D_\theta \nabla^2 \theta.
\end{align*}
\]

(3.18)

The various physical processes modeled by the terms in the r.h.s. of the above equations may be viewed as "generalized chemical reactions" between different families of defects. These reactions include multiplication of dislocations described by the first term of (3.18)\textsuperscript{1}. Multiplication of mobile dislocations also contributes directly to the production of immobile dislocations through the first term of (3.18)\textsuperscript{2}. Grain boundary dislocations also can multiply in a similar way through the second term of (3.18)\textsuperscript{3}. Mobile dislocations can annihilate through the second term of (3.18)\textsuperscript{1} and their "annihilation" gives rise to production of immobile dipoles through the second term of (3.18)\textsuperscript{2}. Grain boundary sliding dislocations can also annihilate through the third term of (3.18)\textsuperscript{3}. Mobile dislocations are trapped by grain boundaries through the first term of (3.18)\textsuperscript{1}. It is important to note that in this case a size effect is included directly through the dependence of $1/d$. These trapped dislocations transform into grain boundary sliding dislocations through the first term of (3.18)\textsuperscript{2}, and junction disclinations through the first term of (3.18)\textsuperscript{4}. Other sources of mobile dislocation include: (i) immobile dipole dislocation through the fourth term of (3.18)\textsuperscript{1}; (ii) activation of dislocation sources by disclination defects through the fifth term of (3.18)\textsuperscript{1}; and (iii) activation of dislocation sources by the pileups of grain boundary dislocations through the sixth term of (3.18)\textsuperscript{1}. There is a corresponding reaction accounting for the diminishing of dislocation dipoles through the third term of (3.18)\textsuperscript{2}. Dislocation dipoles can also disappear during the point defect assisted decay through the fourth term of (3.18)\textsuperscript{2}. We also assume that disclinations in the junctions can be screened by both mobile dislocations and grain boundary sliding dislocations through the first and third terms of (3.18)\textsuperscript{4} respectively. Finally, junction disclinations can lose their activity by absorption of point defects through the fourth term of (3.18)\textsuperscript{4}.

The mobility of the above families of defects is modeled through diffusion-like terms, i.e. the last terms of Eq. (3.18) involving the Laplacians. Such diffusion-like motion may be justified on
the basis of assuming conservation equations for the total defect densities; thus, defects of opposite sign move in opposite directions with the total density obeying diffusion equation. Diffusion like terms may also result by considering coupling effects with vacancies and other types of structural defects not explicitly accounted for in Eqs (3.18) and then “adiabatically eliminating” these internal parameters which are viewed as the fast variables of the system. The “diffusion-like” coefficients \( \left( D_\rho, D_\phi, D_\psi, D_\theta \right) \) should be determined by considering the mobility of the individual defects, their geometry and their interaction with the lattice; and in first approximation one may set \( D_\theta > D_\phi = 0 \). Various simplified versions of Eqs (3.18) may thus be adopted and stationary solutions may be derived along with their stability properties as a function of the grain size.

Alternative evolution equations for defect kinetics in nanopolycrystals may be considered depending on the type of defect populations dominating specific deformation configurations. For example, recent publications focus on the dominant role of nanotwinning. In this case, four different defect populations may be introduced: \( \rho \) – mobile dislocations; \( \theta \) – disclination dipoles (twin fronts); \( \phi \) – twin lamellae; \( \xi \) – sessile Lomer-Cotrell dislocations. Then the following evolution equations may be proposed to model coupled dislocation-nanotwinning processes:

\[
\begin{align*}
\frac{\partial \rho}{\partial t} &= A_\rho \rho - A_\rho \rho^2 - B_1 \rho \phi + F_1 \theta \xi - G_1 \theta \xi \rho - K_\rho \rho \phi + N_\theta \theta \rho + D_\rho \frac{\partial^2 \rho}{\partial x^2}, \\
\frac{\partial \theta}{\partial t} &= B_1 \rho \phi + G_1 \theta \phi \rho - K_\rho \rho \phi - R \theta^2 - D_\theta \frac{\partial^2 \theta}{\partial x^2}, \\
\frac{\partial \phi}{\partial t} &= E_\theta \theta - K_\phi \rho \phi - N_\phi \phi, \\
\frac{\partial \xi}{\partial t} &= A_\xi \rho ^2 - F_2 \theta \xi.
\end{align*}
\]

(3.19)

The physical meaning of the various terms in the r.h.s. of Eqs (3.19)\(_1\)– (3.19)\(_4\) is as follows:

The term \( A_\rho \rho \) describes the activity of dislocation sources. The term with coefficient \( A_\rho \) describes the disappearance of mobile dislocations due to the formation of Lomer-Cotrell sessile dislocations and partly due to annihilation. There is a corresponding term in Eq. (3.19)\(_4\) which describes the input for Lomer-Cotrell dislocations; however the coefficients \( A \)’s in Eqs (3.19)\(_1\) and (3.19)\(_2\) don’t need to be equal and, thus, two rate constants \( A_1 \) and \( A_2 \) are introduced. The term with coefficient \( B_1 \) in (3.19)\(_1\) corresponds to dislocation pile-up formation with a follow-up transformation into mobile dipole fronts \( \theta \), as indicated by the \( B_2 \) term of Eq. (3.19)\(_2\). The \( F_1 \) term describes processes of Lomer-Cotrell barriers dissociation in the field of disclination dipoles and the production of mobile dislocations \( \rho \); the corresponding sink \( F_2 \) term manifests itself in Eq. (3.19)\(_4\). A third order nonlinearity appears in the \( G \) terms which designate complex reactions.
initiated by $\theta$ transforming $\rho$ dislocations into mobile twins ($G_1$) in the vicinity of Lomer-Cottrell dislocations, as well as in the corresponding input for disclination dipoles ($G_2$). The production of new mobile twin fronts (disclination dipoles) $\theta$ is possible due to the reaction between mobile dislocations and twin lamellae – the $K_2$-term in Eq. (3.19)$_2$. This reaction contributes simultaneously to Eq. (3.19)$_1$ (sink term with $K_1$ for $\rho$) and to Eq. (3.19)$_3$ (sink term with $K_3$ for $\varphi$). Mobile twin fronts can destruct twin lamellae resulting to the production of mobile dislocations: the $N_1$-term is responsible for this process and a related sink term in Eq. (3.19)$_3$ involves the coefficient $N_2$. Finally, it is noted that there are also two special reactions which involve the density of one-type of defects only: (i) the $R$-term in Eq. (3.19)$_2$ describing disclination dipole annihilation (no other defects appear as a result of this reaction); and (ii) the $E_0$ source term in Eq. (3.19)$_3$ describing the production of twin lamellae due only to the mobility of twin fronts ($E_0 - v_0$; $v$ designates the velocity of dislocation dipoles).

The next step is to analyze the system of Eq. (3.19)$_1$ - (3.19)$_4$ in the same way as it has been done, for example, by Romanov and Aifantis [37], and work in progress will be reported by these author in a forthcoming publication. In particular, steady state homogeneous solutions may be derived and their stability analysis in the linear and nonlinear regime be considered. Transient soliton-like solutions may be searched for. A combination of Eqs. (3.18) and (3.19) with appropriate modifications and simplifications may also be examined in the case of nc polycrystals where in addition to dislocation structures, nanotwins also occur during deformation.

4. Benchmark Problems

Variants of the aforementioned continuum nanomechanics models have been employed to address several nanoscopic configurations and obtain results in agreement with experiments for which the classical continuum mechanics model could not been used and corresponding molecular dynamics simulations do not suffice for the solution of related boundary value problems.

For eliminating the classical stress and strain singularities at dislocation lines and crack tips, the gradient nanoelasticity model of Eq. (3.5) has been used and corresponding results are given in [26-31]. The same model was used for calculating effective size-dependent elastic moduli, for NC polycrystals [18] in agreement with experiments. The model has also been employed to study wave propagation in nanotubes, in agreement with related results obtained through cumbersome MD simulations [40]. In this connection, Nobel Laureate’s Richard Smalley and Boris Yakobson remark that “the laws of continuum mechanics are amazingly robust for treating even intrinsically discrete objects only a few atoms in diameter”, should be quoted [41].
This view is further implemented here by accounting for bulk-surface interactions and further extending the resulting gradient nanomechanics model beyond elasticity, to consider diffusion and plasticity.

For fitting the nonlinear concentration depth profiles experimentally observed during diffusion in nano-polycrystals, the gradient nano-diffusion model of Eq. (3.11) was used (e.g. [18] and references quoted therein) with reasonable success. In particular, the curvature observed in these profiles and the two diffusion regimes (“slow” through the IC/GB space and the “fast” through the TJ space) could be modeled through the solution of a single higher order diffusion equation.

For fitting the unusual stress-strain graphs for UFG materials exhibiting multiple shear banding, and obtaining the dependence of average shear band thickness on grain size [15], the gradient nanoplasticity model of Eq. (3.16) was used. The same model enhanced with stochastic terms as discussed at the end of Section 3.1 has been used to model with reasonable success serrated size-dependent stress-strain curves in micro/nanopillars [19].

Below, we briefly consider two additional problems. The first problem is concerned with a combination of the gradient nanoelasticity and nanodiffusion model to describe size-dependent spinodal regions for NC materials. The second problem is concerned with the use of Tsallis q-entropy statistics to describe statistical features of serrated stress-strain graphs and corresponding multiple shear bands observed in UFG alloys.

4.1 Size-Dependent Spinodals for NC Materials: When the size of a specimen or grain reduces down to the nanometer level, phase transformations (such as those occurring through the spinodal decomposition mechanism uphill diffusion) and corresponding spinodal or miscibility gaps, depend on the domain size. In this subsection it is illustrated how the ideas of the previous sections can be used to model such observed behavior.

Let us consider a nanograin, at uniform concentration \( \rho_o \) and corresponding elastic displacement \( u_o(x) \), undergoing spinodal decomposition. At the initial stages, assuming small fluctuations for both the concentration and the displacement field, we have

\[
\rho(x,t) = \rho_o + \epsilon \tilde{\rho}(x,t), \quad u(x,t) = u_o(x) + \epsilon \tilde{u}(x,t),
\]

where \( \epsilon (<< 1) \) is a small parameter and \( (\tilde{\rho}, \tilde{u}) \) denote fluctuations. It turns out, by combining the arguments of Sections (3.1) and (3.2), and subsequently applying linear stability analysis to
the resulting governing partial differential equations for the concentration and displacement fields, that [42]

\[
\begin{align*}
\mu \nabla^2 \dot{u} + (\lambda + \mu) \nabla (\nabla \cdot \dot{u}) - c \nabla^2 \left[ \nabla (\nabla \cdot \dot{u}) \right] - (2\mu + 3\lambda) M_o \nabla \left( \dot{\rho} - \ell_e \nabla^4 \dot{\rho} \right) &= 0, \\
\dot{\rho} &= g_2(\rho_0) \nabla^2 \dot{\rho} - g_3(\rho_0) \nabla^4 \dot{\rho} - g_4(\rho_0) \left[ \nabla^2 (\nabla \cdot \dot{u}) - \ell_e \nabla^4 (\nabla \cdot \dot{u}) \right].
\end{align*}
\]  (4.2)

where \( \tilde{M} = \bar{M} \), is the lattice mismatch tensor of the two phases divided by the maximum concentration \( \rho_{\text{max}} \) (in moles per unit volume) when all the accommodating sites in the host material are filled. Furthermore, \( g_i(\rho_0) \) for \( i = 1, 2, \ldots, 6 \) are known functions [42] associated with the diffusion mobility and the material parameters appearing in the free energy density that is given by Eq. (4.5) below. Finally, the internal length \( \ell_e \) is defined in terms of the gradient coefficient \( c \) and the elastic constants of Section 3.1 as \( \ell_e = \sqrt{3c / (2\mu + 3\lambda)} \).

By assuming a finite one-dimensional system of length \( L \), the admissible perturbations have the forms

\[
\begin{align*}
\dot{\rho}(x,t) &= \dot{\rho} e^{\omega t} \cos \left( \frac{n\pi x}{L} \right); \\
u(x,t) &= u e^{\omega t} \sin \left( \frac{n\pi x}{L} \right),
\end{align*}
\]  (4.3)

in order to satisfy proper boundary conditions obtained by the variational formulation of the problem [42]. We can then deduce that uniform concentrations become unstable when

\[
f^* (\rho_0) < - \frac{\kappa \ell_e^4 \left( \frac{\pi}{L} \right)^4 + 12\mu M_o^2 \left[ \left( \frac{\pi}{L} \right)^2 \right]^2 + 3\kappa \frac{2\mu + \lambda}{2\mu + 3\lambda} \left( \frac{\pi}{L} \right)^2}{3 \left( \frac{2\mu + \lambda}{2\mu + 3\lambda} \right) + \ell_e^2 \left( \frac{\pi}{L} \right)^2}.
\]  (4.4)

The function \( f(\rho) \) is the free energy density of a homogeneous and strain-free system of uniform concentration, which is non-convex for systems exhibiting phase separation [43]. This function enters in the total free energy density of the strained nanograin which, in general, has the form

\[
\psi(e, \nabla e, \rho, \nabla \rho) = f(\rho) + \frac{1}{2} \nabla \rho \cdot K \nabla \rho + \frac{1}{2} e \cdot C e + \frac{1}{2} \nabla e \cdot H \nabla e,
\]  (4.5)

where \( K \) and \( H \) are symmetric and positive definite 2\textsuperscript{nd} order tensors which, for simplicity, are assumed to be constants of the form \( K = \kappa I \) and \( H = c I \), while \( C \) is the fourth order elasticity tensor which for isotropic materials is defined as \( C e = 2\mu e + \lambda e I \) (\( e \equiv \text{tr} e \)).
In fact, Eqs. (4.2) are obtained [42] by minimizing the free energy functional given by Eq. (4.5). Next, we assume a usually adopted form for $f(\rho)$, i.e.

$$f(\rho) = G^0 \rho + R \delta \rho_{\text{max}} \left[ \rho \ln \rho + (1-\rho) \ln(1-\rho) \right] + R \delta \rho_{\text{max}} \left[ \alpha \Phi(1-\rho) \right],$$

(4.6)

where $\bar{\rho} = \rho / \rho_{\text{max}}$ ($0 \leq \bar{\rho} \leq 1$) is a normalized concentration, $R$ is the universal gas constant, $\theta$ is the absolute temperature (assumed to be constant), and $G^0$ is a reference value of the chemical potential of the diffusing species. The value of the dimensionless constant $\alpha$ determines the possibility for spinodal decomposition to appear. In particular, only for $\alpha > 2$ the chemical free energy is non-convex with two wells and so the model is able to describe spinodal decomposition.

Substituting Eq.(4.6) into the instability condition given by Eq. (4.4) and applying some algebraic manipulations [42], it turns out that size effects on the spinodal gap width $w$ (in terms of normalized concentration) can be obtained as

$$w = \sqrt{\frac{2\alpha - 4 \pi^2 \left( \frac{\ell_c}{L} \right)^2}{2 \alpha - \pi^2 \left( \frac{\ell_c}{L} \right)^2} \left[ \frac{3 \frac{\mu}{2} + \lambda}{2 \mu + 3 \lambda} + \pi^2 \left( \frac{\ell_c}{L} \right)^2 \right]} - 12 \frac{\mu M_o^2}{R \delta \rho_{\text{max}}} \left[ 1 + \pi^2 \left( \frac{\ell_c}{L} \right)^2 \right]^{1/2},$$

(4.7)

where the internal length $\ell_c$ is associated with the concentration gradient in Eq.(4.5), and it is defined as $\ell_c = \sqrt{\kappa \rho_{\text{max}} / R \theta}$.

Using the values: $R \delta \rho_{\text{max}} = 5.6 \cdot 10^7 Pa$, $\mu = 5 \cdot 10^{10} Pa$, $M_o = 0.017$, $\lambda = 3.93 \cdot 10^{10} Pa$ and $\alpha = 4$ which were computed from the corresponding constants found in [44] at room temperature, the graph of Fig. 4 is obtained for the spinodal gap width $w$ with respect to $L / \ell_c$ and for various values of the ratio $\beta = \ell_c / \ell_c$. 


### Fig. 4: Size effect on the width of the spinodal gap, for various values of the internal lengths ratio $\beta = \ell_c / \ell$. 

#### 4.2 Statistical Features of Serrations and Shear Bands in UFGs:
We analyze the compressive true stress-strain graph of an as-extruded Al-Mg Alloy at strain rate $10^{-2}$ [45] as shown in Fig. 5 (curve A).

**Fig. 5** True compressive stress-strain curves for the as-extruded Al-Mg alloy at room temperature at different strain rates.

The details of the serrations are shown in Fig. 6a.
Fig. 6: a) Detrended stress signal $\Delta Z$ corresponding to stress-strain curve A of Fig. 4. b) Best linear correlation fitting between $\ln q P(Z_i)$ and $(Z_i)^2$ for the detrended stress signal. c) $\log(P(Z_i))$ vs $Z_i$ for the detrended stress time series of curve A (blue circles), the theoretical q-Gaussian (red line) and the normal Gaussian (green line).

The statistical data are interpreted through a Tsallis $q = q_{stat}$ index describing the experimentally measured probability density function (PDF) given by Tsallis $q$-exponential distribution i.e.

$$PDF[(\Delta Z)] = A_q \left[ 1 + (q-1) \beta_q (\Delta Z)^2 \right]^{1/q},$$

where $A_q$ and $\beta_q$ are the normalization constants, $q = q_{stat}$ is the entropic or non-extensivity factor ($q_{stat} \leq 3$) related to the size of the distribution tail and $\Delta Z$ the detrended experimental signal shown in Fig. 6a. This statistical analysis is based on the algorithm described in [46]. We construct the PDF[$\Delta Z$] as follows: The $\Delta Z$ range is subdivided into bins of width $\delta Z$, centered at $Z_i$ so that we can assess the frequency of $\Delta Z$ values that fall within each bin. The resulting histogram is properly normalized (the sum of all probabilities is equal to unity) and the estimated $q$-value corresponds to the best linear fit (maximum correlation coefficient) of the graph.
\[ \ln_q(p(Z_i)) \text{ versus } Z_i^2, \text{ as presented in Fig 6. Then, we compute the } q\text{-Gaussian given by the general equation} \]

\[ G_q(\beta, x) = \sqrt{\beta} / C_q e^{-\beta x^2} \text{ where } C_q = \sqrt{\pi} \cdot \Gamma\left(\frac{3-q}{2(q-1)}\right) / \sqrt{q-1} \cdot \Gamma\left(\frac{1}{q-1}\right), 1 < q < 3 \]

for the obtained \( q_{\text{stat}} \) exponent and for different \( \beta \)-values. After selecting the \( \beta \)-value minimizing the \[ \sum_i [G_{q_{\text{stat}}}(\beta, Z_i) - p(Z_i)]^2 \] [46], we compare the detrended stress time series \( \Delta Z \) (blue circles), the theoretical \( q \)-Gaussian (red line), and the normal Gaussian (green line) as shown in Fig. 6c. The best fitting of the experimental data is obtained for \( q_{\text{stat}} = 1.29 \pm 0.05 \) for a correlation coefficient (cc) equal to 0.9302. When \( q_{\text{stat}} \neq 1 \), then the underlying dynamics is related to hierarchical or (multi)fractal geometry and non-Gaussian statistics [47]. Thus, the underlying dynamics (DSA mechanism) can be related to Tsallis non-extensive statistics, indicating that the interactions between the dislocation motion and solute atoms are of non-Gaussian nature and long ranged.

Another aspect for these UFG Al-Mg Alloys is the occurrence of multiple shear bands at high strain rates [48]. Figure 7a shows a SEM image of shear bands. Corresponding image analysis is conducted to estimate Tsallis \( q_{\text{stat}} \) exponent and the results are shown in Figs.7b,c. Here, the Tsallis \( q_{\text{stat}} \) exponent is used as a statistical index of the image fractal complexity and it was estimated to be equal to 1.312±0.036 (cc=0.9236), revealing the hierarchical and fractal geometry of the shear band network. This fractal geometry indicates a process of far from thermodynamic equilibrium and intense interaction between shear bands [49].
In order to verify the fractal nature of shear band network, we estimated the fractal dimension of the shear band SEM image. For the estimation of the fractal dimension ($D$) we used an improved variation of box counting method (box merge [50]). Scans are made to the data set with a box sized $1/s=1/2$, $1/4$, ..., $1/s_{\text{max}}$ of the size of the box containing the data set. In each scan the number $n$ of the non-empty boxes is counted. The fractal dimension is then calculated from the slope of the linear part of the log($n$) vs log($s$) plot, i.e. $D = \log(n)/\log(s)$.

The results are presented in Fig.8, which shows the logarithm of the number of boxes log($n$) against the logarithm of the box size value of log($s$). The slope which was used for the estimation of the fractal dimension corresponds to the linear scaling regime of the interval log($s$) = 0.5 – 5.5. Above the value of log($s$) = 5.5, a plateau is reached and this is due to the finite (limited) amount of data available. The presence of a small degree of multi-fractality is also noted in the interval log($s$) = 1 – 3. The fractal dimension was found to be $D = 2.3091$. This result suggests that the spatial evolution of multiple shear bands form a complex fractal (slightly multifractal) network. A detailed and more comprehensive analysis for the serrations and shear band fractality observed in UFG materials by using Tsallis q-statistics is provided in a forthcoming article [51].
Fig. 8. Fractal dimension estimation of Fig. 7.

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