A continuum theory of grain size evolution and damage

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[1]   Lithospheric shear localization, as occurs in the formation of tectonic plate boundaries, is often associated with diminished grain size (e.g., mylonites). Grain size reduction is typically attributed to dynamic recrystallization; however, theoretical models of shear localization arising from this hypothesis are problematic because (1) they require the simultaneous action of two creep mechanisms (diffusion and dislocation creep) that occur in different deformation regimes (i.e., in grain size stress space) and (2) the grain growth ("healing") laws employed by these models are derived from normal grain growth or coarsening theory, which are valid in the absence of deformation, although the shear localization setting itself requires deformation. Here we present a new first principles grained-continuum theory, which accounts for both coarsening and damage-induced grain size reduction in a monomineralic assemblage undergoing irrecoverable deformation. Damage per se is the generic process for generation of microcracks, defects, dislocations (including recrystallization), subgrains, nuclei, and cataclastic breakdown of grains. The theory contains coupled macroscopic continuum mechanical and grain-scale statistical components. The continuum level of the theory considers standard mass, momentum, and energy conservation, as well as entropy production, on a statistically averaged grained continuum. The grain-scale element of the theory describes both the evolution of the grain size distribution and mechanisms for both continuous grain growth and discontinuous grain fracture and coalescence. The continuous and discontinuous processes of grain size variation are prescribed by nonequilibrium thermodynamics (in particular, the treatment of entropy production provides the phenomenological laws for grain growth and reduction); grain size evolution thus incorporates the free energy differences between grains, including both grain boundary surface energy (which controls coarsening) and the contribution of deformational work to these free energies (which controls damage). In the absence of deformation, only two mechanisms that increase the average grain size are allowed by the second law of thermodynamics. One mechanism, involving continuous diffusive mass transport from small to large grains, captures the essential components of normal grain growth theories of Lifshitz-Slyosov and Hillert. The second mechanism involves the aggregation of grains and is described using a Smoluchovski formalism. With the inclusion of deformational work and damage, the theory predicts two mechanisms for which the thermodynamic requirement of entropy positivity always forces large grains to shrink and small ones to grow. The first such damage-driven mechanism involving continuous mass transfer from large to small grains tends to homogenize the distribution of grain size toward its initial mean grain size. The second damage mechanism favors the creation of small grains by discontinuous division of larger grains and reduces the mean grain size with time. When considered separately, most of these mechanisms allow for self-similar grain size distributions whose scales (i.e., statistical moments such as the mean, variance, and skewness) can all be described by a single grain scale, such as the mean or maximum. However, the combination of mechanisms, e.g., one that captures the competition between continuous coarsening and mean grain size reduction by breakage, does not generally permit a self-similar solution for the grain size distribution, which contradicts the classic assumption that grain growth laws allowing for both coarsening and recrystallization can be treated with a single grain scale such as the mean size.

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1.   Introduction

1.1.   Background

[2]   The formation of weak and narrow tectonic plate boundaries separating broad, strong plates involves lithospheric shear localization driven invariably by mantle

convection (see reviews by *Tackley* [2000a], *Bercovici et al.* [2000], and *Bercovici* [2003]). Weak zones form and are sustained during deformation, but remain weak after deformation ceases [*Gurnis et al.*, 2000; *Bercovici*, 2003]. The requisite state variable that is both associated with shear localization and permits remnant weak zones could be, for example, increased temperature [*Schubert and Turcotte*, 1972; *Whitehead and Gans*, 1974; *Schubert and Yuen*, 1978; *Fleitout and Froidevaux*, 1980; *Bercovici*, 1996, 1998; *Leloup et al.*, 1999] or void/microcrack density [*Bercovici*, 1998; *Tackley*, 2000b; *Auth et al.*, 2003; *Ogawa*, 2003; *Bercovici et al.*, 2001a, 2001b; *Bercovici and Ricard*, 2003, 2005; *Ricard and Bercovici*, 2003]. However, a well documented feature of lithospheric weak zones is reduced grain size (i.e., mylonites) [*White et al.*, 1980; *Karato*, 1983; *Jin et al.*, 1998; *Furusho and Kanagawa*, 1999]. Lithospheric grain size reduction is typically attributed to dynamic recrystallization whereby grain size is reduced in a high-stress state by the propagation of dislocations [*Karato et al.*, 1980; *Urai et al.*, 1986; *Derby and Ashby*, 1987]. However, theoretical models of shear localization attempting to capture this effect [*Kameyama et al.*, 1997; *Braun et al.*, 1999; *De Bresser et al.*, 1998, 2001; *Montési and Zuber*, 2002; *Montési and Hirth*, 2003] are problematic for several reasons.

[3] First, shear localization requires that an applied stress drives deformation, which induces weakening that subsequently focuses deformation that in turn increases weakening, and so on. However, grain size reduction via dislocation propagation occurs at high stress during dislocation creep which does not permit weakening by grain size reduction since in this rheological regime, viscosity is independent of grain size. Weakening only occurs if the system drops to a lower stress state to undergo diffusion creep, which has a grain-size-dependent viscosity, but does not involve dislocations and thus only permits grain growth. Thus the grain size reduction by imposed stress and deformation, and the grain size weakening that focuses deformation occur in mutually exclusive stress regimes [*De Bresser et al.*, 1998, 2001]. It is possible that these regimes are not exclusive if a nonhomogeneous grain size distribution is allowed; this would permit an effective mixture of regimes, i.e., large grains support dislocation creep and small grains diffusion creep [*Bercovici and Karato*, 2003]. However, recrystallization theories treat mean grain size and not the full grain size distribution.

[4] Second, the grain growth laws employed by recrystallization models are not entirely self-consistent. In particular, the rigorous incorporation of coarsening in a theory is nontrivial since one must account for grain size distributions as well as mean grain size (i.e., coarsening only occurs for nonhomogeneous grain size distributions). However, dynamic recrystallization models [*Kameyama et al.*, 1997; *Braun et al.*, 1999; *De Bresser et al.*, 1998, 2001; *Hall and Parmentier*, 2003; *Montési and Hirth*, 2003; C. Hall and E. M. Parmentier, unpublished manuscript, 2002] generally treat only mean grain size by invoking nondeformational "normal" grain growth theory [*Hillert*, 1965; *Atkinson*, 1988; *Evans et al.*, 2001], which stipulates that grains undergoing coarsening stay in a size distribution that is relatively narrow and self-similar. Although the entire distribution will, during coarsening, drift toward the larger grain size spectrum, the distribution's shape is conserved and its amplitude, variance and mode are all related to one grain size scale which is effectively the average grain size (or alternatively the maximum grain size). Recrystallization theories use this result to justify modeling only the evolution of mean grain size. However, this approach is not self-consistent since such self-similar grain size distributions arise where the only power source is surface energy reduction during coarsening; in actuality, the rapidly deforming shear localization setting involves additional important energy sources such as deformational work.

[5] Third, the driving mechanism for grain reduction in recrystallization theories is an empirically prescribed kinematic condition wherein grain size changes linearly with strain rate [e.g., *Montési and Hirth*, 2003]; as this relation does not arise from basic conservation laws there is no guarantee that energy of the medium is properly conserved (i.e., energy exchange is not considered in the grain growth laws). Moreover, a linear dependence on strain rate might not provide a strong enough nonlinear feedback to generate shear localization. Indeed, localization described by first principles damage theories is typically driven by energy transfer from deformational work to surface energy, or some other thermodynamic manifestation of damage, and is thus a nonlinear function of stress or strain rate [*Ashby and Sammis*, 1990; *Hansen and Schreyer*, 1992; *Lemaitre*, 1992; *Krajcinovic*, 1996; *Lyakhovsky et al.*, 1997; *Bercovici et al.*, 2001a, 2001b; *Bercovici and Ricard*, 2003, 2005; *Ricard and Bercovici*, 2003; *Austin and Evans*, 2007]. (Damage per se is the generic process for generation of microcracks, in both brittle and combined brittle-ductile material, defects, dislocations, including recrystallization, and cataclastic breakdown of grains.) For example, *Bercovici and Ricard* [2005] employed such a damage approach toward both void and grain-size-reducing (or "fineness"-generating) damage; that study demonstrated the profound importance of fineness-generating damage in the formation of plate boundaries from convectively driven flow. Nevertheless, recrystallization and damage theories should be reconcilable at some fundamental level since both involve generating and growing discontinuities (defects, cracks, dislocations, grain boundaries, etc) by an imposed deformation.

[6] In this paper we attempt to unify the damage and grain size evolution approaches in order to obtain a self-consistent theory for lithospheric shear localization. This paper proposes a continuum mechanical theory that also allows for statistical distribution of grain sizes controlled by both coarsening and energy transfer from deformation and damage.

1.2. Hypothesis

[7] The motivation for this theoretical model is to establish a self-consistent continuum theory of a grained medium that allows for grain size evolution in deforming state, thus allowing for the competition between coarsening/grain growth and damage/grain reduction. We assume the medium is a single-phase, single component incompressible viscous material, but made of grains in complete contact with each other along grain boundaries. The grain boundaries themselves have interfacial energy and tension (interfacial energy has units of J m^{-2} and represents either a free energy per unit interfacial area, or a membrane tension. The membrane tension acts to pull on the edges of an interface segment,

tangent to the interface; it thus also has units of force per unit length of interface edge (N m^{-1}). A net force is exerted normal to the interface segment if it has nonzero curvature, and parallel to the segment if surface energy/tension is nonuniform across that area segment. Surface tension and energy differ if there is surface entropy, which occurs if surface tension is a function of temperature or surface chemistry, although that is not the case in this study [see *Leal*, 1992; *Bailyn*, 1994; *Bercovici et al.*, 2001a]. The overall medium differs thus from that of a simple continuum even at the macroscopic scale. The grains also have a continuous size distribution and the occurrence of coarsening or damage is manifest primarily in the evolution of this grain size distribution. For example, during coarsening not all grains grow, but rather larger grains grow at the expense of small ones and thus the grain size distribution (e.g., its mode) drifts to larger grain sizes. Likewise, damage ostensibly causes a decrease in the number of large grains.

[8] In the end, we require two levels of the theory. The macroscopic level contains the continuum mechanical equations of mass, momentum and energy for the averaged medium. Averaging of quantities occurs over a "point" in the continuum which is actually an "infinitesimal" volume containing a statistically meaningful sample of grains (so that while the grain size distribution might depend on position, it does not depend on volume size).

[9] The microscopic level of the theory contains two essential components: First is the kinetic theory of how an individual grain's mass changes depending on the free energies of itself and surrounding grains, and of how the free energy can change by reducing or increasing the number of grains. The second component, is the continuity or evolution equation for grain size distribution, which is coupled to the kinetic equation. As with coarsening theories for "normal" grain growth [*Hillert*, 1965; *Atkinson*, 1988; *Evans et al.*, 2001], the grain size distribution equation can be, in special cases, solved with a similarity approach to describe the distribution shape, as well as the rate its mode shifts in grain size space.

[10] The continuum set of equations imposes the stress and background energy state on the grained medium and thus influences grain growth through deformation-induced damage; since the state (e.g., stress) of the medium changes continuously in space, the grain growth laws also change spatially. Conversely, the change in mean grain size arising from the microscopic equations affects the continuum equations through surface tension effects and through the rheological law, i.e., viscosity is typically grain size dependent for diffusion creep and grain boundary sliding [see *Hirth and Kohlstedt*, 2003]. Thus the theory involves a coupled set of macroscopic/continuum and microscopic/statistical equations (although when we say "microscopic" we mean grain scale). In the end, the full theory involves not only the standard temporal and spatial dimensions, but at least one statistical or grain size dimension as well.

[11] In the following sections we present the derivation of the theory by considering first the statistical representation of the grained continuum and how "continuum" averages are calculated; we then consider continuity equations for grain size distribution as well as kinematics of the model (i.e., having to account for change and flow through both spatial and grain size/statistical dimensions). We will then use these formalisms to derive the continuum conservation laws. The energy equation in particular requires proper thermodynamic treatment and nonequilibrium phenomenological relations (arising from entropy production); from these we derive the kinetic law for grain growth, which requires special consideration to allow for a closed mathematical description that includes both coarsening and damage.

2.   Statistical Description of a Grained Continuum

2.1.   Grain Variables

[12] To derive a continuum theory we consider a control volume δV in which the macroscopic variables and their derivatives are continuous. The dimensions of this volume are small compared to the large-scale process that we intend to describe, but large enough to contain numerous grains so that macroscopic variables can be defined as a statistical average of grain-scale properties.

[13] Except for the grain size $\mathcal{R}$, we denote by an accented variable the properties defined for grains; for example each grain has a volume $\check{v}$ and surface area $\check{A}$. The mass transfer between grains is related to their differences in thermodynamic properties. Each grain thus has its own internal energy $\check{\varepsilon}$, specific entropy $\check{s}$ and chemical potential $\check{\mu}$. Because of the existence of surface energy and tension, γ, each grain also has its own pressure $\check{P}$.

[14] In the present theory we stand to lose little by assuming thermal equilibrium between neighboring grains, i.e., the temperature T is the same for all grains within a volume δV; we are always free to make δV "infinitesimally" small so that temperature gradients over scales much larger than grain size, but still useful in a continuum mechanical sense, are allowed. We also make the reasonable simplifying assumption that the velocity of each grain remains close to the velocity of the center of mass of the control volume δV. The plausibility of this assumption relies on the fact that motion and deformation of the grained continuum must obey a compatibility relations wherein, to remain a continuum, the neighboring grains do not move at different velocities, otherwise gaps and discontinuities would form.

2.2.   Grain Shape

[15] We assume that only one geometrical variable per grain, the grain size $\mathcal{R}$, is enough to characterize each grain geometry. Our theory will therefore not be able to deal with any kind of anisotropy due to crystal fabric. If the grains are generally polyhedral, then $\mathcal{R}$ represents the polyhedral in-radius (the radius of the largest sphere bounded by the polyhedron). All the grain geometrical properties are assumed to be unequivocally related to $\mathcal{R}$, e.g., we assume

$$\check{V} = \frac{4}{3}\Pi\mathcal{R}^3 \text{ and } \check{A} = 4\Pi\mathcal{R}^2, \tag{1}$$

where Π is a geometric factor equal to π for a spherical grain. For simple regular polyhedrons, this geometrical factor is easy to compute; it amounts to $6\sqrt{3}$, 6, $3\sqrt{3}$, 3.79 for tetrahedrons, cubes, octahedrons and isocahedrons, respectively. We assume that grains defined by the same $\mathcal{R}$ are similar enough that they have the same geometrical factor Π and we will use $\Pi = \pi$ for numerical applications (most of the effects of this geometrical factor could also
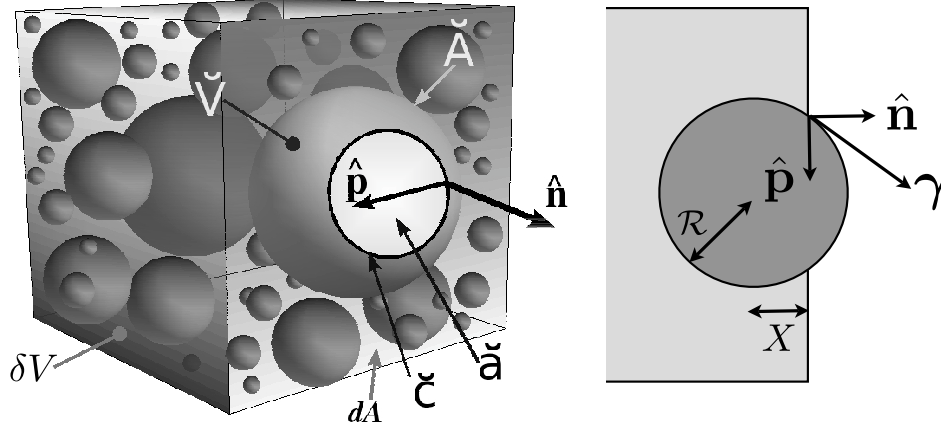
Figure 1. (left) Sketch of a control volume δV of an idealized grained medium illustrating intrinsic grain quantities, such as grain volume $\check{v}$ and grain surface area $\check{A}$. Also shown are properties of the cross section of the grain with one of the control surfaces dA, in particular, the cross-sectional area $\check{A}$, the curve $\check{c}$ marking the intersection between the grain boundary and the cross section, the unit normal to the cross section $\hat{n}$, and the unit vector $\hat{p}$ that is parallel to the cross section but still normal to the intersection curve $\check{c}$. (right) Diagram showing the surface tension force acting along the curve $\check{c}$.

be accounted for by defining an effective surface tension $(\Pi/\pi)\gamma$. Since all the geometrical properties are simple functions of $\mathcal{R}$, all the accented variables, are functions of $\mathcal{R}$, space x and time t.

[16] As discussed below (section 2.4) we need to treat quantities on the cross sections of grains (Figure 1). However, cross sections through polyhedral grains are of any number of possible polygonal shapes depending on the orientation of the cross-sectioning plane relative to the symmetry axes of the polyhedron. Not knowing all grain orientations we can only treat average cross-sectional areas, $\check{A}$, and average lengths of the bounding curves, $\check{c}$ (i.e., averaged over all possible cross-sectioning orientations). We state that a cross section at a distance $x \leq \mathcal{R}$ from the center of a grain, has an average area

$$\check{a} = \Pi\left(\mathcal{R}^2 - X^2\right), \tag{2}$$

and is limited by the bounding curve of length

$$\check{c} = 2\Pi\sqrt{\mathcal{R}^2 - X^2}. \tag{3}$$

We also consider that the total grain surface area $\check{A}$ is sliced off into the surfaces $\check{A}_l$ and $\check{A}_r$, one on the left of the cross section, one on the right, with

$$\check{A}_l = 2\Pi\mathcal{R}^2\left(1 + \frac{X}{\mathcal{R}}\right), \text{ and } \check{A}_r = 2\Pi\mathcal{R}^2\left(1 - \frac{X}{\mathcal{R}}\right), \tag{4}$$

These two equations are only valid for spherical grains but we assume they hold for more complex grain geometries. For convex multifaceted grains they are close approximations.

2.3. Grain Size and Grain Size Distribution

[17] Within a volume element in the continuum δV, there is continuous and convergent distribution of grain sizes, which requires that $\delta V \gg \mathcal{R}_{max}^3$ where $\mathcal{R}_{max}$ is the maxi-

mum grain size for which there are a nonzero number of grains. Since the distribution is continuous, then the number of grains between sizes $\mathcal{R}$ and $\mathcal{R} + d\mathcal{R}$, and per unit volume is $dn = \mathcal{V}_{\mathcal{R}}d\mathcal{R}$, where $\mathcal{V}_{\mathcal{R}}$ is a function of position and time as well as $\mathcal{R}$ (note that dn has units of m^{-3} and $\mathcal{V}_{\mathcal{R}}$ has units of m^{-4}). Thus the total number of grains in a volume element dV at position $\mathbf{x}$ and time t is

$$dN(\mathbf{x}, t) = dV \int_0^\infty \mathcal{V}_{\mathcal{R}}(\mathcal{R}, \mathbf{x}, t)d\mathcal{R}, \tag{5}$$

and thus of course the total number of grains in a larger volume δV is

$$N = \int_{\delta V} \int_0^\infty \mathcal{V}_{\mathcal{R}}d\mathcal{R}dV. \tag{6}$$

[18] It will often be more convenient to use grain mass distributions, $\mathcal{V}_{\mathcal{M}}$, such that the number of grains per unit volume dn with masses between $\check{m}(\mathcal{R})$ and $\check{m}(\mathcal{R} + d\mathcal{R}) = \check{m} + d\check{m}$, is

$$dn = \mathcal{V}_{\mathcal{M}} d\check{m} = \mathcal{V}_{\mathcal{R}} d\mathcal{R}. \tag{7}$$

Since grains are assumed incompressible the density ρ is uniform and constant, thus the grain size distribution $\mathcal{V}_{\mathcal{R}}$ and the grain mass distribution, $\mathcal{V}_{\mathcal{M}}$ (with units of kg^{-1} m^{-3}) are related by

$$\mathcal{V}_{\mathcal{R}} = 4\Pi\mathcal{R}^2\rho\mathcal{V}_{\mathcal{M}}. \tag{8}$$

[19] Grains are assumed to fill all space in the continuum, i.e., there are no gaps between grains; thus the volume of all grains in dV is necessarily also dV which leads to the important normalization conditions, either in terms of volume,

$$\int_0^\infty \check{v}dn = \int_0^\infty \check{v}\mathcal{V}_{\mathcal{R}}d\mathcal{R} = \int_0^\infty \check{v}\mathcal{V}_{\mathcal{M}}d\check{m} = 1, \tag{9}$$

or, since we assume that the density is a constant, in terms of mass

$$\int_0^\infty \check{\mathrm{m}} \, dn = \int_0^\infty \check{\mathrm{m}} \mathcal{V}_\mathcal{R} d\mathcal{R} = \int_0^\infty \check{\mathrm{m}} \mathcal{V}_\mathcal{M} d\check{\mathrm{m}} = \rho, \qquad (10)$$

since $\check{\mathrm{m}} = \rho \check{v}$.

2.4. Surface Quantities and Fluxes

[20] Since our control volume δV is arbitrary, it necessarily cuts through grains at arbitrary positions from the grain centers. We invariably need to treat surface quantities, such as mass fluxes or tractions acting on or through the surface of δV, and thus through various cross sections of grains. Let us consider some such surface quantity on a cross section of grain and with a surface density $\check{\mathrm{q}}$ (such as mass flux per unit area, or force per unit area); $\check{\mathrm{q}}$ is generally a function of $\mathcal{R}$ and can be a scalar or the components of a vector or tensor operating on the normal to the grain's cross section. If the surface dA cuts through a particular grain a distance x from the grain's center, then the amount of this quantity on the grain's cross section is $\check{\mathrm{q}}(\mathcal{R})\check{\mathrm{a}} = \check{\mathrm{q}}(\mathcal{R})\Pi(\mathcal{R}^2 - X^2)$ (see equation (2)). However, dA does not cut through all grains at the same distance x from their centers. The average of this quantity on cross sections of all grains of size $\mathcal{R}$ within the control volumes on either side of the cutting surface dA (see equation (2)) is

$$Q(\mathcal{R}) = \frac{1}{2dX_n} \int_{-dX_n}^{dX_n} \check{\mathrm{q}}(\mathcal{R})\Pi(\mathcal{R}^2 - X^2) dX, \qquad (11)$$

where dX_n is the breadth of the adjacent control volumes on either side of dA (such that each control volume is $dV = dX_n dA$). However, since $\mathcal{R} \ll dX_n$ we only cut through grains whose centers are within $\mathcal{R}$ of the surface dA and thus in fact

$$\begin{aligned} Q(\mathcal{R}) &= \frac{1}{2dX_n} \int_{-\mathcal{R}}^{\mathcal{R}} \check{\mathrm{q}}(\mathcal{R})\Pi(\mathcal{R}^2 - X^2) dX = \frac{1}{2dX_n}\check{\mathrm{q}}(\mathcal{R})\frac{4}{3}\Pi\mathcal{R}^3 \\ &= \frac{1}{2dX_n}\check{\mathrm{q}}(\mathcal{R})\check{v}(\mathcal{R}). \end{aligned}$$
$$(12)$$

[21] There are a total of $2\mathcal{V}_\mathcal{R} d\mathcal{R} dV$ grains of size $\mathcal{R}$ in the two control volumes on either side of the cutting surface; thus the total Q on dA for all grains of all sizes within these volumes is

$$\begin{aligned} Q_{tot} &= 2dV \int_0^\infty \frac{1}{2dX_n}\check{\mathrm{q}}(\mathcal{R})\check{v}(\mathcal{R})\mathcal{V}_\mathcal{R} d\mathcal{R} \\ &= dA \int_0^\infty \check{\mathrm{q}}(\mathcal{R})\check{v}(\mathcal{R})\mathcal{V}_\mathcal{R} d\mathcal{R}. \qquad (13) \end{aligned}$$

Thus if $\check{\mathrm{q}}$ is independent of $\mathcal{R}$ then $Q_{tot} = \check{\mathrm{q}} \, dA$ (see equation (9)); for example if $\check{\mathrm{q}} = 1$ then we have proven that the total cross-sectional area of all grains of all sizes cut by the surface dA is simply dA, which is true since grains fill all space. Invariably, this approach for integrating over volumes and surfaces will be vital for our macroscopic conservation laws.

2.5. Kinematics of Grain Size Distribution

[22] In addition to conservation laws for our continuum, we also require evolution or conservation laws for our grain size distribution. Moreover, to construct conservation laws for properties that depend not only on position and time, but grain size as well, we must discern rates of change consistently, i.e., whether we are considering a rate of change while following a multigrained particle through space (involving the Lagrangian or material time derivative) or the complete rate of change following the particle not only through space but also through grain size "space" as its grain size distribution changes.

[23] In the most general case and in a macroscopically motionless continuum, the change of the number of grains of sizes between $\mathcal{R}$ and $\mathcal{R} + d\mathcal{R}$ can be caused by two different processes. First, grain populations can move continuously through $\mathcal{R}$ space since grains in the size interval between $\mathcal{R}$ and $\mathcal{R} + d\mathcal{R}$ can gain or lose mass and hence move to a neighboring interval of sizes. This continuous process involves proximal exchange between grain populations and occurs via diffusive mass transfer between grains. Second, the population of a given size can increase because two smaller grains have coalesced or can decrease by the division of a grain. This process involves discontinuous transfer between remote population intervals (e.g., breakage of grains in half causes population exchange from the interval centered on $\mathcal{R}$ to the one centered on $\mathcal{R}/2$). This discontinuous and remote exchange occurs during (1) cataclastic fragmentation, (2) when subgrain boundaries appear [Hobbs, 1968] and (3) when a finite sized grain is nucleated. We refer to the former process as continuous exchange between proximal populations, and the latter process as discontinuous exchange between remote populations.

[24] The continuity equation for $\mathcal{V}_\mathcal{R}$ can be derived by considering the rate of change of the total number of grains δn between sizes $\mathcal{R}_1$ and $\mathcal{R}_2 > \mathcal{R}_1$ in the fixed volume element δV

$$\frac{d\delta n}{dt} = \frac{d}{dt}\left(\int_{\delta V}\int_{\mathcal{R}_1}^{\mathcal{R}_2}\mathcal{V}_\mathcal{R} d\mathcal{R} dV\right) = \left(\int_{\delta V}\int_{\mathcal{R}_1}^{\mathcal{R}_2}\frac{\partial \mathcal{V}_\mathcal{R}}{\partial t} d\mathcal{R} dV\right).$$
$$(14)$$

[25] The change of this number of grains can be due to transport of different grain populations into δV by the macroscopic velocity $\mathbf{v}$, and by change in grain number within the volume δV (by both continuous and discontinuous exchange between populations of different sized grains). These transport processes together lead to

$$\begin{aligned} \frac{d\delta n}{dt} = &-\int_{\delta V}\int_{\mathcal{R}_1}^{\mathcal{R}_2}\boldsymbol{\nabla}\cdot(\mathcal{V}_\mathcal{R}\mathbf{v}) d\mathcal{R} dV \\ &-\int_{\delta V}\left[\mathcal{V}_\mathcal{R}\dot{\mathcal{R}}\right]_{\mathcal{R}_1}^{\mathcal{R}_2} dV + \int_{\delta V}\int_{\mathcal{R}_1}^{\mathcal{R}_2}\Gamma_\mathcal{R} d\mathcal{R} dV. \qquad (15) \end{aligned}$$

[26] In the second term on the right side, we used the fact that, in a time dt, the number of grains lost from the population between $\mathcal{R}_1$ and $\mathcal{R}_2$ to the population with $\mathcal{R} > \mathcal{R}_2$ is $\left[\mathcal{V}_\mathcal{R}\dot{\mathcal{R}}dt\right]_{\mathcal{R}_2} dV$ (and likewise the number of grains added from the population with $\mathcal{R} < \mathcal{R}_1$ is $\left[\mathcal{V}_\mathcal{R}\dot{\mathcal{R}}dt\right]_{\mathcal{R}_1} dV$); [see also Hillert, 1965; Atkinson, 1988].

In the last term of (15), $\Gamma_{\mathcal{R}}$ is the rate at which grains of size $\mathcal{R}$ are added or removed by discontinuous processes (i.e., breaking or coalescence). Accounting for the fact that δV is arbitrary, and taking the limit that $\mathcal{R}_2 - \mathcal{R}_1 \to 0$ (or really $\mathcal{R}_2 - \mathcal{R}_1 = d\mathcal{R}$), (15) yields the continuity equation for $\mathcal{V}_{\mathcal{R}}$

$$\frac{D\mathcal{V}_{\mathcal{R}}}{Dt} + \mathcal{V}_{\mathcal{R}}\boldsymbol{\nabla}\cdot\mathbf{v} + \frac{\partial(\dot{\mathcal{R}}\mathcal{V}_{\mathcal{R}})}{\partial\mathcal{R}} = \frac{d\mathcal{V}_{\mathcal{R}}}{dt} + \mathcal{V}_{\mathcal{R}}\boldsymbol{\nabla}\cdot\mathbf{v} + \mathcal{V}_{\mathcal{R}}\frac{\partial\dot{\mathcal{R}}}{\partial\mathcal{R}} = \Gamma_{\mathcal{R}}, \tag{16}$$

[see also *Hillert*, 1965; *Atkinson*, 1988; *Voorhees*, 1992]. In this equation, we introduced the usual Lagrangian derivative, which is also the total derivative holding $\mathcal{R}$ constant

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + (\mathbf{v}\cdot\boldsymbol{\nabla}) = \left(\frac{d}{dt}\right)_{\mathcal{R}}, \tag{17}$$

and therefore, the full time derivative is

$$\frac{d}{dt} = \frac{D}{Dt} + \dot{\mathcal{R}}\frac{\partial}{\partial\mathcal{R}}, \tag{18}$$

which is a formalism we will adopt throughout this paper. Equation (16) is the four-dimensional (4-D) generalization of the usual conservation equation in three dimensions (3-D); to wit, in the 4-D space $\mathbf{r}_4 = (x, y, z, \mathcal{R})$, the velocity is $\mathbf{v}_4 = (v_x, v_y, v_z, \dot{\mathcal{R}})$, the gradient operator is $\boldsymbol{\nabla}_4 = (\partial/\partial x, \partial/\partial y, \partial/\partial z, \partial/\partial\mathcal{R})$ and (16) is expressed by

$$\frac{\partial\mathcal{V}_{\mathcal{R}}}{\partial t} + \boldsymbol{\nabla}_4\cdot(\mathcal{V}_{\mathcal{R}}\mathbf{v}_4) = \Gamma_{\mathcal{R}}. \tag{19}$$

[27] The evolution of the grain mass distribution is similarly obtained, and is expressed by

$$\frac{\partial\mathcal{V}_{\mathcal{M}}}{\partial t} + \boldsymbol{\nabla}\cdot(\mathbf{v}\mathcal{V}_{\mathcal{M}}) + \frac{\partial(\dot{\breve{m}}\mathcal{V}_{\mathcal{M}})}{\partial\breve{m}} = \Gamma_{\mathcal{M}}, \tag{20}$$

where, by definition $\Gamma_{\mathcal{R}}d\mathcal{R} = \Gamma_{\mathcal{M}}d\breve{m}$, hence,

$$\Gamma_{\mathcal{M}} = \frac{\Gamma_{\mathcal{R}}}{4\Pi\rho\mathcal{R}^2}. \tag{21}$$

[28] Let us next consider the rate of change of a granular quantity $\breve{\theta}(\mathcal{R}, \mathbf{x}, t)$, such as, for example, the mass or internal energy of a grain of size $\mathcal{R}$. The total amount of this quantity in all grains and in a finite volume δV within our continuum is

$$\Theta = \int_{\delta V}\int_0^\infty \breve{\theta}(\mathcal{R}, \mathbf{x}, t)\mathcal{V}_{\mathcal{R}}\,d\mathcal{R}\,dV. \tag{22}$$

The rate of change of Θ following the closed and deformable volume δV is

$$\frac{D\Theta}{Dt} = \int_{\delta V}\int_0^\infty \left(\frac{\partial(\breve{\theta}\mathcal{V}_{\mathcal{R}})}{\partial t} + \boldsymbol{\nabla}\cdot\left(\mathbf{v}\breve{\theta}\mathcal{V}_{\mathcal{R}}\right)\right)d\mathcal{R}\,dV. \tag{23}$$

Using (16) and (18), equation (23) becomes

$$\frac{D\Theta}{Dt} = \int_{\delta V}\left(\int_0^\infty\left[\frac{d\breve{\theta}}{dt}\mathcal{V}_{\mathcal{R}} + \breve{\theta}\Gamma_{\mathcal{R}}\right]d\mathcal{R} - \left[\breve{\theta}\dot{\mathcal{R}}\mathcal{V}_{\mathcal{R}}\right]_{\mathcal{R}=0}^\infty\right)dV. \tag{24}$$

[29] The last quantity inside the volume integral involves loss of $\breve{\theta}$ by flux of grain populations (e.g., by grain growth or grain reduction) beyond the tails of the distribution $\mathcal{V}_{\mathcal{R}}$. However, except for the actual grain number itself, physical granular quantities (e.g., grain mass, grain surface area, grain energy, grain entropy, etc.), vanish for vanishing grain size, hence $\breve{\theta}\dot{\mathcal{R}}\mathcal{V}_{\mathcal{R}} \to 0$ for $\mathcal{R} \to 0$. In contrast, we assume that the grain size distribution itself converges for grain sizes much less than the control volume size such that $\mathcal{V}_{\mathcal{R}} \to 0$ and also $\breve{\theta}\dot{\mathcal{R}}\mathcal{V}_{\mathcal{R}} \to 0$, as $\mathcal{R} \to \delta V^{1/3}$. In total, the fluxes through the distribution tails are assumed 0 and (24) becomes simply

$$\frac{D\Theta}{Dt} = \int_{\delta V}\int_0^\infty\left(\frac{d\breve{\theta}}{dt}\mathcal{V}_{\mathcal{R}} + \breve{\theta}\Gamma_{\mathcal{R}}\right)d\mathcal{R}\,dV. \tag{25}$$

[30] Equation (25) relates a macroscopic change to the sum of the ''microscopic'' continuous and discontinuous processes of mass exchange between grain populations. For example, consider $\breve{\theta} = \breve{m}$ and $\Theta = M$ the total mass of δV, which is a conserved quantity. From (25) we obtain

$$\frac{DM}{Dt} = 0 = \int_{\delta V}\int_0^\infty\left[\frac{d\breve{m}}{dt}\mathcal{V}_{\mathcal{R}} + \breve{m}\Gamma_{\mathcal{R}}\right]d\mathcal{R}\,dV. \tag{26}$$

[31] We assume the discontinuous processes of grain sticking or breaking occur instantaneously, i.e., over a much shorter time scale than diffusive exchange between grains. Therefore, since any instantaneous exchange of populations must conserve mass independently of other slower processes (i.e., the time scales for these processes are separable), we write

$$\int_0^\infty \breve{m}\Gamma_{\mathcal{R}}\,d\mathcal{R} = \int_0^\infty \breve{m}\Gamma_{\mathcal{M}}\,d\breve{m} = 0 \tag{27}$$

where the volume integral is removed since δV is arbitrary. Given (27), equation (26) implies that

$$\int_0^\infty \frac{d\breve{m}}{dt}\mathcal{V}_{\mathcal{R}}\,d\mathcal{R} = \int_0^\infty \dot{\mathcal{R}}\frac{\partial\breve{m}}{\partial\mathcal{R}}\mathcal{V}_{\mathcal{R}} = 0, \tag{28}$$

since $\breve{m} = \breve{m}(\mathcal{R})$ and we have again used the fact that δV is arbitrary.

[32] In total, the evolution of grain size distribution is governed by (16) (or alternatively (19) or (20)), and grain quantities are conserved according to (25). However, these laws require expressions for $\dot{\mathcal{R}}$ and $\Gamma_{\mathcal{R}}$ (or alternatively $\dot{\breve{m}}$ and $\Gamma_{\mathcal{M}}$) that govern continuous grain growth and discontinuous exchange between grain size populations by breaking or coalescence. Thus a major goal of this paper is to use the constraints of nonequilibrium macroscopic

thermodynamics, in particular the positivity of the entropy sources to specify the quantities $\dot{\mathcal{R}}$ and $\Gamma_{\mathcal{R}}$ (or $\overset{\smile}{\mathsf{m}}$ and $\Gamma_{\mathcal{M}}$).

3. Mass, Momentum Conservation, and Dynamic Equilibrium

3.1. Mass Conservation

[33] The expression for mass conservation is straightforward. Since grains move at velocity $\mathbf{v}$, the mass flux through a grain's cross section $\overset{\smile}{\mathsf{A}}$ normal to $\hat{\mathbf{n}}$ is

$$\overset{\smile}{\mathsf{q}} = \rho\mathbf{v} \cdot \hat{\mathbf{n}} \tag{29}$$

Using (13), the total mass flux across the surface δA is therefore $\mathbf{J} = \int_{\delta A} dA \int_0^\infty \rho\mathbf{v} \cdot \hat{\mathbf{n}}\overset{\smile}{\mathsf{v}}\mathcal{V}_{\mathcal{R}}d\mathcal{R}$, and since $\rho\mathbf{v} \cdot \hat{\mathbf{n}}$ is independent of $\mathcal{R}$, the normalization condition (9) leads to

$$\mathbf{J} = \rho\int_{\delta A} \mathbf{v} \cdot \hat{\mathbf{n}}dA = \rho\int_{\delta V} \boldsymbol{\nabla} \cdot \mathbf{v}dV. \tag{30}$$

[34] Since we assume the material to be incompressible, then $\mathbf{J} = 0$ which, since δV is an arbitrary volume, requires

$$\boldsymbol{\nabla} \cdot \mathbf{v} = 0, \tag{31}$$

as expected and we can therefore remove the terms in $\boldsymbol{\nabla} \cdot \mathbf{v}$ in the grain size and grain mass evolution equations (16) and (20).

3.2. Momentum Conservation

[35] In this paper we consider only the case of dynamic equilibrium, i.e., where the forces are all in balance and acceleration is negligible. This setting is relevant for viscous creeping motion, elastostatic equilibrium, and slow viscoelastic motion wherein the time scales considered are much longer than those for "quaking" behavior or propagation of elastic waves. The absence of an explicit time derivative in the momentum equation, does not mean that the system is in steady state. The macroscopic rheology and interfacial surface tension ultimately depend on the grain size distribution, which is an explicit function of time and evolves even in the absence of deformation. For the application toward lithospheric shear localization on mantle convection and plate boundary evolution time scales, we mainly consider subsolidus viscous flow. The addition of acceleration and inertia for shorter time scale problems of faulting and earthquakes should involve minor effort since we equate the continuum velocity and the grain velocity, and thus momentum and its material derivative (i.e., acceleration) are easily established. In the present paper, the law of conservation of momentum requires only that no gaps appear between deforming grains and that all forces balance; thus we must simply account for body, surface and line forces on the volume δV. The model, therefore, does not account for open voids, secondary phases or components that limit intergrain contact, such as might occur in fault gouge, porous matrices and in polymineralic assemblages. These would be important for the next generation of this theory but also introduce extensive complexity and additional degrees of freedom.

[36] In the following, we use the terms "static" and "dynamic" to describe situations in which the macroscopic velocities are either zero (static) or nonzero (dynamic). None of these situations is, however, truly static or steady. Even in the case without macroscopic deformation, which we call "static", the grain size distribution evolves at a microscopic level and induces changes in surface tension, rheology and energy dissipation that affect the macroscopic pressure and temperature fields. The only truly static system would be a nondeforming medium made of a single grain.

3.3. Body Forces

[37] The body force on δV is due to the action of a body force per unit mass vector $\mathbf{g}$ (typically gravitational acceleration) acting on the mass of all grains of all sizes and is thus

$$\mathbf{F}_b = \int_{\delta V}\int_0^\infty \overset{\smile}{\mathsf{m}}\mathbf{g}\mathcal{V}_{\mathcal{R}}d\mathcal{R}dV = \int_{\delta V}\rho\mathbf{g}dV, \tag{32}$$

as expected, and where we have used (10) and the fact that $\mathbf{g}$ is independent of grain size $\mathcal{R}$.

3.4. Surface Forces

[38] The surface force acting on the area δA surrounding δV is due to the total force acting on all cross sections of grains cut by the surface. If $\underline{\overset{\smile}{\boldsymbol{\sigma}}}$ is the full stress tensor acting on one grain of size $\mathcal{R}$, then the force on the grain's cross section $\overset{\smile}{\mathsf{A}}$ is $\hat{\mathbf{n}} \cdot \underline{\overset{\smile}{\boldsymbol{\sigma}}}\overset{\smile}{\mathsf{a}}$, and thus, using (13) in which $\hat{\mathbf{n}} \cdot \underline{\overset{\smile}{\boldsymbol{\sigma}}}$ is substituted for $\overset{\smile}{\mathsf{q}}$, the force on all grains of all sizes intersected by δA is

$$\mathbf{F}_s = \int_{\delta A}\int_0^\infty \hat{\mathbf{n}} \cdot \underline{\overset{\smile}{\boldsymbol{\sigma}}}\overset{\smile}{\mathsf{v}}\mathcal{V}_{\mathcal{R}}d\mathcal{R}dA. \tag{33}$$

[39] If we define $\underline{\boldsymbol{\sigma}}$ as the volume average of $\underline{\overset{\smile}{\boldsymbol{\sigma}}}$ such that

$$\underline{\boldsymbol{\sigma}} = \int_0^\infty \underline{\overset{\smile}{\boldsymbol{\sigma}}}\overset{\smile}{\mathsf{v}}\mathcal{V}_{\mathcal{R}}d\mathcal{R}, \tag{34}$$

then

$$\mathbf{F}_s = \int_{\delta A}\hat{\mathbf{n}} \cdot \underline{\boldsymbol{\sigma}}dA = \int_{\delta V}\boldsymbol{\nabla} \cdot \underline{\boldsymbol{\sigma}}dV, \tag{35}$$

as expected.

[40] The above result is independent of the constitutive relationship for $\underline{\overset{\smile}{\boldsymbol{\sigma}}}$. We can decompose stress into isotropic and deviatoric parts by writing as usual that

$$\underline{\overset{\smile}{\boldsymbol{\sigma}}} = \overset{\smile}{P}\underline{I} + \underline{\overset{\smile}{\boldsymbol{\tau}}}, \tag{36}$$

where $\overset{\smile}{P}$ and $\underline{\overset{\smile}{\boldsymbol{\tau}}}$ are the pressure and deviatoric stress in a grain. The statistical volume-averaged stress, from (34), is of course simply

$$\underline{\boldsymbol{\sigma}} = -P\underline{I} + \underline{\boldsymbol{\tau}}, \tag{37}$$

where P and $\underline{\boldsymbol{\tau}}$ are the averaged pressure and deviatoric stress.

[41] Our model assumes that all grains of the same radius are affected by the same stress and the same strain rate $\underline{\overset{\smile}{\boldsymbol{\tau}}}$ and $\underline{\overset{\smile}{\mathsf{e}}}$. The constitutive law for $\underline{\overset{\smile}{\boldsymbol{\tau}}}$ is therefore

$$\underline{\overset{\smile}{\boldsymbol{\tau}}} = 2\overset{\smile}{\eta}\underline{\overset{\smile}{\mathsf{e}}}, \tag{38}$$

where the grain viscosity $\breve{\eta}(\mathcal{R}, \breve{\underline{e}})$ is a function of both grain size and strain rate as the grain deformation may result from various mechanisms acting simultaneously (e.g., diffusion creep, dislocation creep, etc.). We also require that the grain-scale strain rate $\breve{\underline{e}}$ averaged over all grain sizes in the control volume δV corresponds to the macroscopic strain rate, and thus that

$$\dot{\underline{e}} = \int_0^\infty \breve{\underline{e}} \breve{v} \mathcal{V}_\mathcal{R} d\mathcal{R}. \tag{39}$$

As the continuum is incompressible and as we assume isotropy, the constitutive relation between the macroscopic stress and strain rate (34) and (39) can be written as $\underline{\tau} = 2\eta\dot{\underline{e}}$ where we must define the macroscopic viscosity η as the ratio of two second invariants, $\eta = \tau/(2\dot{e})$, where $\tau = \sqrt{\underline{\tau} : \underline{\tau}}$ and $\dot{e} = \sqrt{\dot{\underline{e}} : \dot{\underline{e}}}$; this leads to

$$\eta = \frac{\left[\left(\int_0^\infty \breve{\eta}\breve{\underline{e}}\breve{v}\mathcal{V}_\mathcal{R} d\mathcal{R}\right) : \left(\int_0^\infty \breve{\eta}\breve{\underline{e}}\breve{v}\mathcal{V}_\mathcal{R} d\mathcal{R}\right)\right]^{1/2}}{\left[\left(\int_0^\infty \breve{\underline{e}}\breve{v}\mathcal{V}_\mathcal{R} d\mathcal{R}\right) : \left(\int_0^\infty \breve{\underline{e}}\breve{v}\mathcal{V}_\mathcal{R} d\mathcal{R}\right)\right]^{1/2}}. \tag{40}$$

Thus the macroscopic viscosity η is generally a function of grain size and strain rate ($\mathcal{V}_\mathcal{R}$ and $\breve{\underline{e}}$ are explicitly present in (40) and furthermore, $\breve{\eta}$ is likely to be a function of $\mathcal{R}$ and $\breve{\underline{e}}$). Of course, if the strain rate is uniform across all grains, then we will find that $\eta = \int_0^\infty \breve{\eta}\breve{v}\mathcal{V}_\mathcal{R} d\mathcal{R}$ while if the stress is uniform across all grain then we will find that $\eta = \left[\int_0^\infty (1/\breve{\eta})\breve{v}\mathcal{V}_\mathcal{R} d\mathcal{R}\right]^{-1}$. More complex averaging schemes (e.g., by using a variational estimates as in the work of *Hashin and Shtrikman* [1963]) would give a viscosity estimate in between these two bounds.

[42] In most classical rheological treatments [e.g., *Poirier*, 1991; *Hirth and Kohlstedt*, 2003], the macroscopic viscosity is only related to the average grain size and the average stress. However, equations (40) indicates that the viscosity is a statistical average where, according to its size, each grain may be in a different deformation regime (diffusion creep, grain boundary sliding, dislocation creep, etc.). The macroscopic viscosity is therefore different from the viscosity of the average grain size.

3.5. Surface Tension and Line Forces

[43] As noted by *Bercovici et al.* [2001a], surface tension on the interface between two phases or as in the theory presented here, on grain boundaries, manifests itself as a line force acting on the surface δA of the control volume δV. In particular, the intersections of grain boundaries with the surface of the control volume are curves on which surface tension pulls outward with a line force (force per unit length) of magnitude γ, which is in fact simply the surface tension. Consider the control volume's surface intersecting a grain of size $\mathcal{R}$ a distance X from the center of the grain. The intersection curve has a mean length $\breve{c} = 2\Pi\sqrt{\mathcal{R}^2 - X^2}$ (see (3)). At all points on the intersection curve, the surface tension pulls both normal to this curve and tangent to the grain boundary itself. By symmetry, only the component of the line force vector perpendicular to the control surface element, with amplitude $\tilde{\gamma}_n = \gamma\sqrt{\mathcal{R}^2 - X^2}/\mathcal{R}$ has a nonzero

average (see Figure 1). The average line force for all grains of size $\mathcal{R}$ cut by, and within a distance dX_n of, the control surface is thus (see section 2.4),

$$\frac{1}{2dX_n} \int_{-\mathcal{R}}^{+\mathcal{R}} \breve{c}\tilde{\gamma}_n\hat{\mathbf{n}}dX = \frac{1}{2dX_n} \int_{-\mathcal{R}}^{+\mathcal{R}} 2\Pi\frac{\mathcal{R}^2 - X^2}{\mathcal{R}}\gamma\hat{\mathbf{n}}dX$$
$$= \frac{1}{2dX_n}\frac{2\gamma}{\mathcal{R}}\breve{v}\hat{\mathbf{n}}. \tag{41}$$

[44] The total force on all grains of all sizes and arbitrary distances from the cutting surface dA can be deduced by replacing $\breve{\mathbf{q}}$ with $(2\gamma/\mathcal{R})\hat{\mathbf{n}}$ in equations (11)–(13), which leads to the total surface tension force acting on the control surface δA of

$$\mathbf{F}_l = \int_{\delta A} \int_0^\infty \gamma\breve{\mathcal{K}}\hat{\mathbf{n}}\breve{v}\mathcal{V}_\mathcal{R} d\mathcal{R} dA, \tag{42}$$

where

$$\breve{\mathcal{K}} = \frac{2}{\mathcal{R}} = \frac{d\breve{\mathsf{A}}}{d\breve{v}} = \frac{2}{3}\frac{\breve{\mathsf{A}}}{\breve{v}}, \tag{43}$$

is the net curvature of a grain of size $\mathcal{R}$. Assuming that surface tension γ is independent of grain size $\mathcal{R}$, and defining the volume-averaged net grain boundary curvature as

$$\mathcal{K} = \int_0^\infty \breve{\mathcal{K}}\breve{v}\mathcal{V}_\mathcal{R} d\mathcal{R}, \tag{44}$$

we obtain

$$\mathbf{F}_l = \int_{\delta A} \gamma\mathcal{K}\hat{\mathbf{n}}dA = \int_{\delta V} \boldsymbol{\nabla}(\gamma\mathcal{K})dV. \tag{45}$$

3.6. Total Force Equation

[45] Balancing the net forces on the volume δV from equations (32), (35), and (45), and noting that the volume δV is arbitrary, we obtain the equilibrium equation

$$0 = \rho\mathbf{g} + \boldsymbol{\nabla} \cdot \boldsymbol{\sigma} + \boldsymbol{\nabla}(\gamma\mathcal{K}) \tag{46}$$

which has the expected form of a continuum mechanical equilibrium equation, with the exception of the interfacial surface tension component. The presence of the interfacial surface tension term in the momentum equation, and that it manifests itself as the gradient of a potential, corresponds to previous work on two-phase continuum theory with interfacial effects [e.g., *Bercovici et al.*, 2001a].

[46] Although the continuum force equation describes macroscopic motion of a volume of many grains, it is still coupled to the grain-scale dynamics. While the body force term is independent of the physics occurring at the grain scale, the surface force term depends on grain-scale dynamics through at least the rheology, and possibly through other effects if there is grain boundary slippage leading to stress couples (which we assume to not occur in this theory). The line force or surface tension term depends on the grain-scale physics through the average grain

curvature $\mathcal{K}$ which obviously changes as the grain size distribution changes.

4. Thermodynamics and Energy Conservation

[47] Damage theory is generally predicated on the assumption that the internal energy of a continuum $E(S, \rho, \underline{\mathcal{D}})$ is not only based on the usual state variables S and ρ (entropy and density), but also on a scalar or tensorial "damage" variable $\underline{\mathcal{D}}$ [e.g., *Lemaitre*, 1992; *Krajcinovic*, 1996; *Houlsby and Puzrin*, 2000; *Lyakhovsky et al.*, 2005]. The rheological properties of the material are related to the damage variable, whose evolution is constrained by the 2nd law of thermodynamics. Although this damage formalism is general, the physical manifestation of damage itself is not readily identified and the experimental measure of $\underline{\mathcal{D}}$ is indirect (e.g., the damage tensor can be adjusted in order for the theory to reproduce a given set of deformation experiments, but not measured directly by microscopic analysis). Moreover, while the conjugate variables of S and ρ are clearly T and P, respectively, the conjugate to $\underline{\mathcal{D}}$ is physically ambiguous and only defined as the partial derivative of free energy with respect to $\underline{\mathcal{D}}$.

[48] In our approach (as well and in our earlier work on two-phase damage theory [see *Bercovici et al.*, 2001a, 2001b; *Bercovici and Ricard*, 2003, 2005; *Ricard and Bercovici*, 2003]), however, the damage variable is readily identified with the amount of interfacial surface energy present in the system. In this case the internal energy is naturally written as $E(S, \rho, \alpha)$ where $\alpha = \int_0^\infty \breve{\mathsf{A}} \mathcal{V}_\mathcal{R} d\mathcal{R}$ is the interfacial or grain boundary area density (area per unit volume) and is the isotropic equivalent to the damage variable $\underline{\mathcal{D}}$. In our model, damage corresponds to a measurable property (grain boundary area), and its conjugate variable is clearly identified as interfacial surface tension γ. Our model in its present form cannot account for anisotropy because we have assumed that grains are isotropic (both crystallographically and morphologically) such that the resulting interfacial area density α is a scalar; however, this assumption can be relaxed by including other grain characteristics leading to the tensorial form of α termed by *Bercovici et al.* [2001a] the fabric $\underline{\alpha}$ [see also *Drew*, 1971; *Drew and Segel*, 1971].

4.1. Thermodynamics of an Ensemble of Grains

[49] The total intrinsic energy contained in volume δV (i.e., the total energy less the kinetic energy due to bulk motion of the entire volume, which is neglected to be consistent with the assumption that acceleration is negligible) is given by the sum of volumetric internal energy and total surface grain boundary energy:

$$E = \int_{\delta V} \int_0^\infty \left(\breve{\mathsf{m}} \breve{\varepsilon} + \gamma \breve{\mathsf{A}} \right) \mathcal{V}_\mathcal{R} d\mathcal{R} dV, \qquad (47)$$

in which $\breve{\varepsilon}$ is the specific volumetric internal energy of a grain of size $\mathcal{R}$ (notice that since $\breve{\mathsf{A}}$ is the grain surface, the sum of all grain surfaces is two times what could be defined as total surface of grain interfaces: our definition of surface energy may thus be half of what an experimentalist would call surface energy). We assume that surface tension is temperature independent so that no irreversible surface

energy (in which surface entropy goes as $-d\gamma/dT$) is present in the system [*Desjonquères and Spanjaard*, 1993; *Bailyn*, 1994; *Bercovici et al.*, 2001a]. Surface entropy could be readily included [see *Bercovici et al.*, 2001a] but it is superfluous to the intentions of this theory. The rate of change of total energy in the volume δV is thus (using (25))

$$\frac{DE}{Dt} = \int_{\delta V} \int_0^\infty \left[\left(\frac{d(\breve{\mathsf{m}}\breve{\varepsilon})}{dt} + \gamma \frac{d\breve{\mathsf{A}}}{dt} \right) \mathcal{V}_\mathcal{R} + \Gamma_\mathcal{R} \left(\breve{\mathsf{m}}\breve{\varepsilon} + \gamma \breve{\mathsf{A}} \right) \right] d\mathcal{R} dV. \qquad (48)$$

[50] We can also write a Gibbs relation for the increment in total energy E as the sum of all energy increments for all grains. During a time interval dt, the total energy changes not only because of the continuous and diffusive exchange of mass and energy between grains, but also because of the discontinuous exchange (from breaking and sticking) leading to a change in number of grains of size $\mathcal{R}$ given by $\Gamma_\mathcal{R} dt$. The increment in total energy is therefore

$$dE = \int_{\delta V} \int_0^\infty \left(T d\breve{S} - \breve{P} d\breve{\mathsf{v}} + \breve{\mu} d\breve{\mathsf{m}} + \gamma d\breve{\mathsf{A}} \right) \mathcal{V}_\mathcal{R} d\mathcal{R} dV$$
$$+ \int_{\delta V} \int_0^\infty \left(T\breve{S} - \breve{P}\breve{\mathsf{v}} + \breve{\mu}\breve{\mathsf{m}} + \gamma \breve{\mathsf{A}} \right) \Gamma_\mathcal{R} dt d\mathcal{R} dV, \qquad (49)$$

where T is the temperature (assumed to be uniform in the volume δV, as discussed in section 2.1), $\breve{S}, \breve{P}$ and $\breve{\mu}$ are the grain entropy, pressure and chemical potential, respectively. Notice that we assume that the only mechanical exchange of work $-\breve{P}\breve{\mathsf{v}}$ is through the pressure forces and therefore that the energy exchange due to the deviatoric stresses will ultimately appear in a dissipative term and in the generation of damage. The elastic strain energy is therefore ignored in our model.

[51] The extrinsic grain quantities of entropy and volume can be written in terms of grain mass; i.e., $\breve{S} = \breve{\mathsf{m}}\breve{s}$ and $\breve{\mathsf{v}} = \breve{\mathsf{m}}/\rho$ where $\breve{s}$ is the grain specific entropy (entropy per mass); with these expressions and the above Gibbs relation (49), the total increment in internal energy per unit time dE/dt is

$$\frac{DE}{Dt} = \int_{\delta V} \int_0^\infty \left[\left(T \frac{d(\breve{\mathsf{m}}\breve{s})}{dt} - \breve{P} \frac{d(\breve{\mathsf{m}}/\rho)}{dt} + \breve{\mu} \frac{d\breve{\mathsf{m}}}{dt} + \gamma \frac{d\breve{\mathsf{A}}}{dt} \right) \mathcal{V}_\mathcal{R} \right.$$
$$\left. + \left(\breve{\mathsf{m}} \left(T\breve{s} - \frac{\breve{P}}{\rho} + \breve{\mu} \right) + \gamma \breve{\mathsf{A}} \right) \Gamma_\mathcal{R} \right] d\mathcal{R} dV, \qquad (50)$$

where note that by (18), $dE/dt = DE/Dt$ since E is a function of space and time, but not grain size $\mathcal{R}$. Subtracting (50) from (48), we obtain

$$\int_{\delta V} \int_0^\infty \left[\breve{\mathsf{m}} \left(\frac{d\breve{\varepsilon}}{dt} - T \frac{d\breve{s}}{dt} + \breve{P} \frac{d(1/\rho)}{dt} \right) \mathcal{V}_\mathcal{R} \right.$$
$$\left. + \left(\frac{d\breve{\mathsf{m}}}{dt} \mathcal{V}_\mathcal{R} + \breve{\mathsf{m}}\Gamma_\mathcal{R} \right) \left(\breve{\varepsilon} - T\breve{s} + \frac{\breve{P}}{\rho} - \breve{\mu} \right) \right] d\mathcal{R} dV = 0, \qquad (51)$$

where, even though we have been assuming incompressibility, we temporarily and for the sake of exposition retain terms involving derivatives of ρ. Since equation (51) must hold for any grain size distribution and kinetic law, there is

no way for the term proportional to $\check{m}$ to vanish (i.e., since $\check{m} > 0$) other than requiring the internal energy to obey

$$d\check{\varepsilon} = Td\check{s} - \check{P}d(1/\rho). \qquad (52)$$

[52] The term proportional to $(\mathcal{V}_{\mathcal{R}}d\check{m}/dt + \check{m}\Gamma_{\mathcal{R}})$ cancels according to mass conservation (26) provided that $\check{\varepsilon} - T\check{s} + \check{P}/\rho - \check{\mu}$ is at most a constant independent of $\mathcal{R}$. This constant represents the background energy state that is the same for all neighboring grains within the volume δV. Since only differences in chemical potential affect grain size evolution, there is no loss of generality in adopting the classical relation for the chemical potential

$$\check{\mu} = \check{\varepsilon} - T\check{s} + \check{P}/\rho. \qquad (53)$$

Since the grains are assumed viscous, the only direct and reversible mechanical contribution to the chemical potential is $\check{P}/\rho$; if elasticity were to be incorporated, the chemical potential would also include the product of stress and strain tensors [see, e.g., *Shimizu*, 1992]. Finally, if we also employ incompressibility, then we find $d\check{\varepsilon} = Td\check{s}$ and by expansion of scales (given local thermal equilibrium) $\check{\varepsilon} = T\check{s}$, which leads quite simply to

$$\check{\mu} = \check{P}/\rho. \qquad (54)$$

4.2. Energy Conservation in a Grained Continuum

[53] In our thermodynamic treatment so far we have considered the energy of an arbitrary volume δV in our continuum without describing any fluxes through its surface; nor were we specific about the nature of the volume itself, i.e., whether it is fixed or moving in space, whether its surface is closed and deformable, or open and fixed. Here we consider the complete energy equation considering all fluxes and sources of energy on our volume, which we choose to be fixed in space with open boundaries.

[54] The rate of change of total energy of this fixed and open volume is dictated by fluxes of energy through its surface, work done on the volume (by body, surface and line forces) and internal energy or heat production. Again, since we assume dynamic equilibrium (e.g., creeping flow) kinetic energy is considered negligible.

4.2.1. Energy Fluxes

[55] The flux of internal energy associated with mass transport through the cross section of a grain of size $\mathcal{R}$ cut by the area element dA with unit normal $\hat{\mathbf{n}}$ and a distance X from the grain's center is $\rho\check{\varepsilon}\mathbf{v} \cdot \hat{\mathbf{n}}\Pi(\mathcal{R}^2 - X^2)$. Following the development of (13) (in particular using $\check{q} = \rho\check{\varepsilon}\mathbf{v} \cdot \hat{\mathbf{n}}$), the flux of internal energy going through the control surface is

$$\mathbf{J}_{\varepsilon} = \int_{\delta A}\int_0^{\infty} \check{m}\check{\varepsilon}\mathbf{v} \cdot \hat{\mathbf{n}}\mathcal{V}_{\mathcal{R}}d\mathcal{R}dA. \qquad (55)$$

[56] In addition to the flux of internal energy $\mathbf{J}_{\varepsilon}$, a flux of surface energy $\mathbf{J}_{\gamma}$ is also present. The surface area of grain sliced off by dA is $2\Pi\mathcal{R}^2(1 + X/\mathcal{R})$ (see (4)) and thus the rate at which this surface varies with X is $2\Pi\mathcal{R}\dot{X} = -2\Pi\mathcal{R}\mathbf{v} \cdot \hat{\mathbf{n}}$. Therefore the average flux of surface energy γ for all grains of size $\mathcal{R}$ within $dX_n > \mathcal{R}$ of the cutting

surface is (following a similar line of reasoning leading to (12) and (13))

$$\frac{1}{2dX_n}\int_{-\mathcal{R}}^{+\mathcal{R}} \gamma 2\Pi\mathcal{R}\mathbf{v} \cdot \hat{\mathbf{n}}dX = \frac{1}{2dX_n}\gamma 4\Pi\mathcal{R}^2\mathbf{v} \cdot \hat{\mathbf{n}} = \frac{1}{2dX_n}\gamma\check{A}\mathbf{v} \cdot \hat{\mathbf{n}}. \qquad (56)$$

[57] The total flux of surface energy through the cross sections of all grains in the volume $2dX_ndA$ cut by dA is $\int_0^{\infty} \gamma\check{A}\mathbf{v} \cdot \hat{\mathbf{n}}\mathcal{V}_{\mathcal{R}}d\mathcal{R}dA$, and therefore the total flux through the control volume's surface δA is

$$\mathbf{J}_{\gamma} = \int_{\delta A}\int_0^{\infty} \gamma\check{A}\mathbf{v} \cdot \hat{\mathbf{n}}\mathcal{V}_{\mathcal{R}}d\mathcal{R}dA. \qquad (57)$$

4.2.2. Mechanical Work

[58] The rate of body force work done on δV is quite simply the sum of work done by the body force per mass, e.g., gravity, on all grain masses, i.e.,

$$W_b = \int_{\delta V}\int_0^{\infty} \check{m}\mathbf{v} \cdot \mathbf{g}\mathcal{V}_{\mathcal{R}}d\mathcal{R}dV. \qquad (58)$$

The rate of surface work done by stresses (using (13) and substituting $\hat{\mathbf{n}} \cdot \underline{\underline{\sigma}} \cdot \mathbf{v}$ for $\check{q}$) is

$$W_s = \int_{\delta A}\int_0^{\infty} \hat{\mathbf{n}} \cdot \underline{\underline{\sigma}} \cdot \mathbf{v}\check{v}\mathcal{V}_{\mathcal{R}}d\mathcal{R}dA. \qquad (59)$$

[59] The derivation of the rate of work done by surface tension follows section 3.5. The surface tension force is applied on the curve $\check{c}$ that delineates the intersection of a grain surface and the control surface. Both components of surface tension parallel and perpendicular to the control surface do work when a grain crosses the control surface. However, since there is statistically the same number of grains with their centers on either side of the control surface, the work of the surface tension components parallel to the control surface cancel when averaged. The rate of work done by the component of surface tension perpendicular to the control surface on a segment $d\ell$ of the curve marking the cross section of the grain boundary with the cutting surface (at a distance X from the grain center) is $\tilde{\gamma}_n\mathbf{v} \cdot \hat{\mathbf{n}}\,d\ell$ in which $\tilde{\gamma}_n = \gamma\sqrt{\mathcal{R}^2 - X^2}/\mathcal{R}$. The integral of this element of work over the length of the intersecting curve $\check{c} = 2\Pi\sqrt{\mathcal{R}^2 - X^2}$ is thus $\gamma 2\Pi\mathbf{v} \cdot \hat{\mathbf{n}}(\mathcal{R}^2 - X^2)/\mathcal{R}$. The total rate of work on all grains of all sizes and arbitrary distances from the cutting surface dA can be deduced by using $\check{q} = (2\gamma/\mathcal{R})\mathbf{v} \cdot \hat{\mathbf{n}}$ (see also (43)) in equations (11)–(13), which leads to the total surface tension work acting on the control surface δA of

$$W_l = \int_{\delta A}\int_0^{\infty} \gamma\check{K}\mathbf{v} \cdot \hat{\mathbf{n}}\check{v}\mathcal{V}_{\mathcal{R}}d\mathcal{R}dA. \qquad (60)$$

4.2.3. Rate of Energy Change

[60] We now write the total rate of change in intrinsic energy (energy less the kinetic energy).

$$\frac{\partial E}{\partial t} = \int_{\delta V}\int_0^{\infty}\left(\frac{\partial(\check{m}\check{\varepsilon}\mathcal{V}_{\mathcal{R}})}{\partial t} + \gamma\frac{\partial(\check{A}\mathcal{V}_{\mathcal{R}})}{\partial t}\right)d\mathcal{R}dV$$

$$= -\mathbf{J}_{\varepsilon} - \mathbf{J}_{\gamma} + W_b + W_s + W_l - \int_{\delta A} \mathbf{q}dA + \int_{\delta V} \mathcal{Q}dV, \quad (61)$$

where $\mathbf{q}$ is the heat flux vector and $\mathcal{Q}$ is internal heat production, both assumed grain size independent. The fluxes and work terms are given by (55)–(60).

[61] With the divergence theorem, the surface integrals of this energy balance are expressed as volume integrals over δV; as this volume is arbitrary we obtain

$$\int_0^\infty \left(\frac{\partial(\check{m}\check{\varepsilon}\mathcal{V}_{\mathcal{R}})}{\partial t} + \gamma \frac{\partial\left(\check{A}\mathcal{V}_{\mathcal{R}}\right)}{\partial t} \right) d\mathcal{R} = -\int_0^\infty \boldsymbol{\nabla}$$
$$\cdot \left[\left(\check{m}\check{\varepsilon} + \gamma\check{A}\right)\mathbf{v}\mathcal{V}_{\mathcal{R}} \right] d\mathcal{R} + \int_0^\infty \check{m}\mathbf{v}\cdot\mathbf{g}\mathcal{V}_{\mathcal{R}}d\mathcal{R} + \int_0^\infty \boldsymbol{\nabla}$$
$$\cdot \left[\left(\underline{\underline{\boldsymbol{\sigma}}}\cdot\mathbf{v} + \gamma\check{\mathcal{K}}\mathbf{v}\right)\check{v}\mathcal{V}_{\mathcal{R}} \right] d\mathcal{R} - \boldsymbol{\nabla}\cdot\mathbf{q} + \mathcal{Q}, \qquad (62)$$

Using the relation for the material derivative of grain-averaged quantities (see (23)–(25)), and the force equilibrium equation (46), the energy equation can be recast as

$$\int_0^\infty \left[\left(\frac{d(\check{m}\check{\varepsilon})}{dt} + \gamma\frac{d\check{A}}{dt} \right)\mathcal{V}_{\mathcal{R}} + \left(\check{m}\check{\varepsilon} + \gamma\check{A}\right)\Gamma_{\mathcal{R}} \right] d\mathcal{R}$$
$$= \Psi - \boldsymbol{\nabla}\cdot\mathbf{q} + \mathcal{Q}, \qquad (63)$$

where

$$\Psi = \underline{\underline{\boldsymbol{\tau}}} : \boldsymbol{\nabla}\mathbf{v} = \underline{\underline{\boldsymbol{\tau}}} : \underline{\underline{\dot{e}}}, \qquad (64)$$

is the rate of deformational work; note that we have removed the volume integral since δV is arbitrary. Equation (63) relates the microscopic energy exchange (left side) to the macroscopic energy exchange (right side).

4.3. Entropy Production

[62] The internal entropy production in a volume δV is the total rate of entropy increase less the external entropy input from entropy flux through the volume's surface δA; by the 2nd law of thermodynamics the internal entropy production is necessarily greater than zero, i.e.,

$$\frac{DS}{Dt} + \int_{\delta A} \mathbf{J}_s\cdot\hat{\mathbf{n}}dA \geq 0, \qquad (65)$$

where $\mathbf{J}_s$ is the entropy flux not associated with mass transport (which is accounted for already in the material derivative). Typically non-mass flux entropy loss is only due to heat loss and so

$$\mathbf{J}_s = \mathbf{q}/T. \qquad (66)$$

[63] After writing entropy S as the statistical average over grains, using again the relation between material derivative and grain average quantities (see (23)–(25)) and Green's divergence theorem for the entropy flux term, (65) becomes

$$\int_0^\infty \left(\frac{d(\check{m}\check{s})}{dt}\mathcal{V}_{\mathcal{R}} + \check{m}\check{s}\Gamma_{\mathcal{R}} \right) d\mathcal{R} + \boldsymbol{\nabla}\cdot(\mathbf{q}/T) \geq 0, \qquad (67)$$

where the arbitrary volume integral as been removed (as already discussed in (23)–(25), $\check{m}\check{s}\dot{\mathcal{R}}\mathcal{V}_{\mathcal{R}}$ vanishes as $\mathcal{R}\to 0$

and $\mathcal{R}\to\infty$) Another relation involving entropy change can be derived from energy conservation, (63) using (52) and (53)

$$\int_0^\infty \left[\left(T\frac{d(\check{m}\check{s})}{dt} - \check{P}\frac{d\check{v}}{dt} + \check{\mu}\frac{d\check{m}}{dt} + \gamma\frac{d\check{A}}{dt} \right)\mathcal{V}_{\mathcal{R}} \right.$$
$$\left. + \left(\check{m}\left(\check{\mu} + T\check{s} - \frac{\check{P}}{\rho}\right) + \gamma\check{A} \right)\Gamma_{\mathcal{R}} \right] d\mathcal{R} = \Psi - \boldsymbol{\nabla}\cdot\mathbf{q} + \mathcal{Q}. \quad (68)$$

[64] By subtracting (68) from T times the entropy equation, (67), we arrive at

$$\int_0^\infty \left[\left(\left(\check{P} - \gamma\check{\mathcal{K}}\right)\frac{d\check{v}}{dt} - \check{\mu}\frac{d\check{m}}{dt} \right)\mathcal{V}_{\mathcal{R}} - \check{m}\left(\check{\mu} - \frac{\check{P}}{\rho} + \frac{3}{2}\frac{\gamma\check{\mathcal{K}}}{\rho} \right)\Gamma_{\mathcal{R}} \right] d\mathcal{R}$$
$$+ \Psi + \mathcal{Q} - \frac{1}{T}\mathbf{q}\cdot\boldsymbol{\nabla}T \geq 0, \qquad (69)$$

where we have also introduced the grain curvature $\check{\mathcal{K}}$ using (43). Equation (69) reveals the standard relations that Ψ and $\mathcal{Q}$ are positive definite, and that for the heat flux term to be positive definite, $\mathbf{q}$ and $-\boldsymbol{\nabla}T$ must be proportional as suggested by Fourier's law of heat conduction.

[65] The term proportional to $\mathcal{V}_{\mathcal{R}}$ in (69) could have been reduced by taking into account that $\check{m} = \rho\check{v}$, but it has been temporarily retained to illustrate three important points.

[66] First, the factor $\check{P} - \gamma\check{\mathcal{K}}$ represents the grain pressure in excess of what is caused by the surface tension of the grain boundary squeezing the grain, and thus is the pressure acting to expand the grain and generate a nonzero $d\check{v}/dt$. However, excess pressure should in fact be written as the grain pressure in excess of both surface tension from the grain boundary and background pressure external to the grain, otherwise the grain pressure would do no work to expand the grain if surface tension were zero; i.e., the excess pressure is really $\check{P} - \bar{P} - \gamma\check{\mathcal{K}}$ where $\bar{P}$ is the background pressure. There is no loss of generality in replacing $\check{P} - \gamma\check{\mathcal{K}}$ with $\check{P} - \bar{P} - \gamma\check{\mathcal{K}}$ in the entropy production equation (69) since $\bar{P}$ is independent of grain size (being the pressure averaged over all grains in the volume) and its contribution to entropy production only involves a term proportional to $\int_0^\infty (d\check{v}/dt)\mathcal{V}_{\mathcal{R}}d\mathcal{R} = D(1)/Dt = 0$ (see equation (9)). If the pressure difference exactly balanced surface tension then it would satisfy Laplace's condition for static equilibrium between a pressure drop across a curved interface and the surface tension on the interface. However if the grain pressure, say, exceeded the sum of the external pressure and the surface tension, then, in simple cases (see the more general discussion about damage in section 7) it should act mechanically to expand the grain and thus the term $\left(\check{P} - \bar{P} - \gamma\check{\mathcal{K}}\right)d\check{v}/dt$ should be positive definite.

[67] Second, the term in (69) proportional to $d\check{m}/dt$ represents entropy production from grain growth. The term itself is readily interpreted if rewritten as $(\check{\mu} - \bar{\mu})d\check{m}/dt$ where $\bar{\mu}$ is a background mean chemical potential (again this factor would make no contribution to the integral in (69) for our incompressible medium; see equation (10)). This term shows that if a grain's chemical potential $\check{\mu}$ is larger than that of its surroundings, then it will lose mass

which migrates down chemical potential gradients; thus $-(\breve{\mu} - \bar{\mu})d\breve{m}/dt$ should also be generally positive definite (see section 7).

[68] Third, the last term proportional to $\Gamma_{\mathcal{R}}$ indicates that it is also possible to change the entropy by simply changing the number of grains. Each grain carries a surface energy term $3\gamma\breve{\mathcal{K}}\breve{m}/2\rho = \gamma\breve{A}$ and since, contrary to grain masses, grain surfaces are not conserved during the coalescence or breaking of grains, the change in grain number affects the entropy balance.

[69] Equation (69) is used to develop grain growth laws for both coarsening and damage. However, to simplify matters we employ our assumption that the medium is incompressible and thus $\breve{\mu} = \breve{P}/\rho$ (see (54)). For simplicity we also assume that there is no heat generation ($\mathcal{Q} = 0$) and no heat flux ($\mathbf{q} = 0$; e.g., the medium is insulated or isothermal). With these assumptions taken together, (69) eventually reduces to

$$\int_0^\infty \left(-\gamma\breve{\mathcal{K}}\frac{d\breve{m}}{dt}\mathcal{V}_{\mathcal{R}} - \frac{3}{2}\gamma\breve{\mathcal{K}}\breve{m}\Gamma_{\mathcal{R}}\right)d\mathcal{R} + \rho\Psi \geq 0, \quad (70)$$

where we have multiplied (69) by ρ. Equation (70) represents a fundamental relationship for our combined damage and coarsening theory in that it expresses the internal entropy production by deformational work, and changes in grain size or grain number.

[70] Using the definition of the curvature (43) and the expression for the rate of change of a granular quantity (25), the positivity of internal entropy production can also be written simply as

$$-\gamma\frac{D\alpha}{Dt} + \Psi \geq 0, \quad (71)$$

where α is the grain boundary area per unit volume [see also *Bercovici et al.*, 2001a],

$$\alpha = \int_0^\infty \breve{A}\mathcal{V}_{\mathcal{R}}d\mathcal{R}. \quad (72)$$

[71] Equation (71) clearly shows that in the absence of deformation, the grain boundary area per unit volume must decrease (e.g., by evolving toward less numerous but larger grains). It is only in the presence of damage $\Psi > 0$ that a reduction of the grain boundary area per unit volume is possible.

[72] In the following, we first consider the entropy terms related to continuous (coarsening) and discontinuous (breaking/sticking) exchanges of grain mass between grain populations as separate and independent. We then show that the potential coupling of these processes together with the effects of deformational work is what leads to a theory of combined coarsening and damage. In the evolution equation for grain size distribution, we do not consider the advection term and we equate D/Dt with $\partial/\partial t$. This simplification is valid in the static case (i.e., when $\mathbf{v} = 0$) but also in a simple shearing experiment (i.e., with $\mathbf{v} \neq 0$ and $\Psi \neq 0$, which is necessary for damage to occur), since during simple

shearing the grain size distribution remains uniform along the direction of advection (i.e., the gradient in grain size is perpendicular to the damaged shear bands).

5. Static Grain Growth by Continuous Processes

5.1. Grain Coarsening by Diffusion

[73] We first consider static grain growth (i.e., no damage and/or $\Psi = 0$). We assume that the grain population can only change by continuous exchange of mass between grains in the absence of discontinuous processes (coalescence or fracture) that allow remote exchange between grain size populations. The changes in grain mass $d\breve{m}/dt$, must satisfy the constraints of entropy positivity, (70), mass and distribution conservation, (28) and (16), with $\Psi = \Gamma_{\mathcal{R}} = 0$,

$$\int_0^\infty -\gamma\breve{\mathcal{K}}\frac{d\breve{m}}{dt}\mathcal{V}_{\mathcal{R}}d\mathcal{R} \geq 0, \quad (73a)$$

$$\int_0^\infty \frac{d\breve{m}}{dt}\mathcal{V}_{\mathcal{R}}d\mathcal{R} = 0, \quad (73b)$$

$$\frac{\partial\mathcal{V}_{\mathcal{R}}}{\partial t} + \frac{\partial(\dot{\mathcal{R}}\mathcal{V}_{\mathcal{R}})}{\partial\mathcal{R}} = 0. \quad (73c)$$

[74] The system of equations (73) can be used to develop the well known equations for static grain growth [*Hillert*, 1965].

[75] We make the usual assumption of linear nonequilibrium thermodynamics, that "thermodynamic forces" acting on grains, i.e., the $\gamma\breve{\mathcal{K}}$, and "thermodynamic fluxes", i.e., the $d\breve{m}/dt$, are simply coupled through a linear system of phenomenological relations [*de Groot and Mazur*, 1984]. In our case, the forces and fluxes are all scalar quantities, but there are as many forces and fluxes as there are grains. The change in mass of one grain of radius $\mathcal{R}$ depends on its interactions with all the other grains of radii $\mathcal{R}'$. The linear system of phenomenological relations appears therefore as a convolution over the grain space distribution:

$$\frac{d\breve{m}(\mathcal{R})}{dt} = \gamma\int_0^\infty G^c(\mathcal{R}, \mathcal{R}')\breve{\mathcal{K}}(\mathcal{R}')\mathcal{V}_{\mathcal{R}}(\mathcal{R}')d\mathcal{R}' \quad (74)$$

where $G^c(\mathcal{R}, \mathcal{R}')$ is the *grain interaction function* that determines how much the chemical potential or pressure of a grain of size $\mathcal{R}'$ affects the growth rate of a grain of size $\mathcal{R}$. In other words, a single grain's growth is coupled to the growth and reduction of all grains, and thus is influenced by the chemical potential (or pressure) of all neighboring grains (proximity of grains is not relevant since information about pressure differences and fluctuations is propagated at the speed of sound such that the medium essentially starts to respond to these changes instantaneously everywhere). The function $G^c(\mathcal{R}, \mathcal{R}')$ can also be interpreted as the conductivity (or inverse resistance) of mass flux driven by chemical potential (e.g., G^c is invariably related to chemical diffusivity).

[76] Although $G^c(\mathcal{R}, \mathcal{R}')$ cannot be uniquely determined there are several constraints that reveal its basic properties.

First, according to Onsager's reciprocal relations [*de Groot and Mazur*, 1984], the phenomenological matrix $G^c(\mathcal{R}, \mathcal{R}')$ is symmetric,

$$G^c(\mathcal{R}, \mathcal{R}') = G^c(\mathcal{R}', \mathcal{R}). \tag{75}$$

(in other words, the physical principle relating the free energies of grains of size $\mathcal{R}'$ to the growth of grains of size $\mathcal{R}$ is the same as that which relates the free energies of grains of size $\mathcal{R}$ to the growth of grains of size $\mathcal{R}'$). Second, the matrix $G^c(\mathcal{R}, \mathcal{R}^{s'})$ and the relation (74) must satisfy the mass conservation equation (73b). This implies that

$$\int_0^\infty \frac{d\breve{m}(\mathcal{R})}{dt} \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R} = \gamma \int_0^\infty \breve{\mathcal{K}}' dn' \int_0^\infty G^c(\mathcal{R}, \mathcal{R}') dn = 0, \tag{76}$$

where we use the abbreviated notation $dn = \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R}$, $dn' = \mathcal{V}_\mathcal{R}(\mathcal{R}') d\mathcal{R}'$, $\breve{\mathcal{K}} = \breve{\mathcal{K}}(\mathcal{R})$ and $\breve{\mathcal{K}}' = \breve{\mathcal{K}}(\mathcal{R}')$ (we will frequently adopt this convention in equations involving two or more integrals). For (76) to be true for any grain size distribution, the interaction function $G^c(\mathcal{R}', \mathcal{R})$ should satisfy

$$\int_0^\infty G^c(\mathcal{R}, \mathcal{R}') dn = \int_0^\infty G^c(\mathcal{R}', \mathcal{R}) dn = 0, \tag{77}$$

where we also use the symmetry of $G^c(\mathcal{R}, \mathcal{R}')$. Therefore we can rewrite the evolution of grain size (74), as

$$\frac{d\breve{m}(\mathcal{R})}{dt} = \gamma \int_0^\infty G^c(\mathcal{R}, \mathcal{R}') \left[\breve{\mathcal{K}}' - \breve{\mathcal{K}} \right] dn', \tag{78}$$

which, because of the symmetry of $G^c(\mathcal{R}, \mathcal{R}')$, satisfies the total conservation of mass (73b).

[77] With the conditions (73a), (75) and (78), we can readily show that coarsening dissipation rate is

$$-\int_0^\infty \gamma \breve{\mathcal{K}} \frac{d\breve{m}}{dt} \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R}$$
$$= -\gamma^2 \iint_0^\infty G^c(\mathcal{R}, \mathcal{R}') \left[\breve{\mathcal{K}}' - \breve{\mathcal{K}} \right] \breve{\mathcal{K}} dn dn'. \tag{79}$$

The double integral on the right side of (79) is invariant to an interchange of the integration variables $\mathcal{R}$ and $\mathcal{R}'$. Therefore, given the symmetry of $G^c(\mathcal{R}, \mathcal{R}')$, we can expressed (79) as

$$-\int_0^\infty \gamma \breve{\mathcal{K}} \frac{d\breve{m}}{dt} \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R}$$
$$= \frac{1}{2} \gamma^2 \iint_0^\infty G^c(\mathcal{R}, \mathcal{R}') \left[\breve{\mathcal{K}}' - \breve{\mathcal{K}} \right]^2 dn dn' \geq 0. \tag{80}$$

[78] Therefore the positivity of the entropy sources requires that $G^c(\mathcal{R}, \mathcal{R}')$ is a positive function. (Note that linear nonequilibrium thermodynamics usually introduces positive definite operators, analogous to a positive definite matrices; however, the particular form of coarsening dissipation given by (80) involves coupling of only positive quantities $\left[\breve{\mathcal{K}}' - \breve{\mathcal{K}} \right]^2$, and therefore only requires the positivity of $G^c(\mathcal{R}, \mathcal{R}')$.) An obvious (but not necessary) form that satisfies all the above constraints on $G^c(\mathcal{R}, \mathcal{R}')$ is a quadratic product between functions of $\mathcal{R}$ and $\mathcal{R}'$; e.g.,

$$G^c(\mathcal{R}, \mathcal{R}') = B(\mathcal{R})B(\mathcal{R}'), \tag{81}$$

where $B(\mathcal{R})$ is any function of grain size and we have left off a "diagonal" term proportional to $\delta(\mathcal{R} - \mathcal{R}')$, which is needed to satisfy (77), because it makes no contribution to the grain growth or entropy production (dissipation) equations given the pervasive factor of $\breve{\mathcal{K}}' - \breve{\mathcal{K}}$. Adopting this form of $G^c(\mathcal{R}, \mathcal{R}')$, the grain growth law (78) now becomes very simply

$$\frac{d\breve{m}(\mathcal{R})}{dt} = \gamma \beta(\mathcal{R}) \left[\overline{\mathcal{K}} - \breve{\mathcal{K}}(\mathcal{R}) \right], \tag{82}$$

where

$$\beta(\mathcal{R}) = B(\mathcal{R}) \int_0^\infty B(\mathcal{R}') \mathcal{V}_\mathcal{R}(\mathcal{R}') d\mathcal{R}', \tag{83}$$

is introduced for the sake of mathematical brevity, and we generally define for any granular quantity $\breve{\theta}$ the weighted average quantity $\overline{\theta}$

$$\overline{\theta} = \frac{\int_0^\infty \breve{\theta}(\mathcal{R}')B(\mathcal{R}')\mathcal{V}_\mathcal{R}(\mathcal{R}')d\mathcal{R}'}{\int_0^\infty B(\mathcal{R}')\mathcal{V}_\mathcal{R}(\mathcal{R}')d\mathcal{R}'}. \tag{84}$$

Notice that since $\mathcal{V}_\mathcal{R}$ is time and space dependent, so are β and $\overline{\mathcal{K}}$. This eventually reduces to the simple standard grain growth laws often employed in coarsening problems and Ostwald-Ripening [e.g., *Lifshitz and Slyozov*, 1961; *Wagner*, 1961; *Hillert*, 1965; *Atkinson*, 1988; *Evans et al.*, 2001; *Voorhees*, 1992].

5.2. Example Solutions for Coarsening

[79] Although analytic and numerical treatments of coarsening can be found elsewhere [e.g., *Collet and Goudon*, 2000], here we show a simple example using a power law relation for $B(\mathcal{R})$, which is consistent with previous studies of coarsening [e.g., *Lifshitz and Slyozov*, 1961; *Hillert*, 1965]; we therefore write

$$B(\mathcal{R}) = \sqrt{4\Pi\rho} B_0 \mathcal{R}^p, \tag{85}$$

where the exponent p can be either positive or negative. This expression for $B(\mathcal{R})$ and (82), $\dot{\mathcal{R}}$ becomes

$$\dot{\mathcal{R}} = 2\gamma B_0^2 I_p R^{p-2} \left(\overline{\mathcal{R}^{-1}} - \mathcal{R}^{-1} \right), \tag{86}$$

where B_0^2 has units of $m^{7-2p} \, kg^{-1} \, s$ and

$$I_p = \int_0^\infty \mathcal{R}^p \mathcal{V}_\mathcal{R} d\mathcal{R}. \tag{87}$$

[80] Defining an average time-dependent grain size $\langle \mathcal{R} \rangle = (\overline{\mathcal{R}^{-1}})^{-1}$ and the similarity variable $u = \mathcal{R}/\langle \mathcal{R} \rangle$, we show in
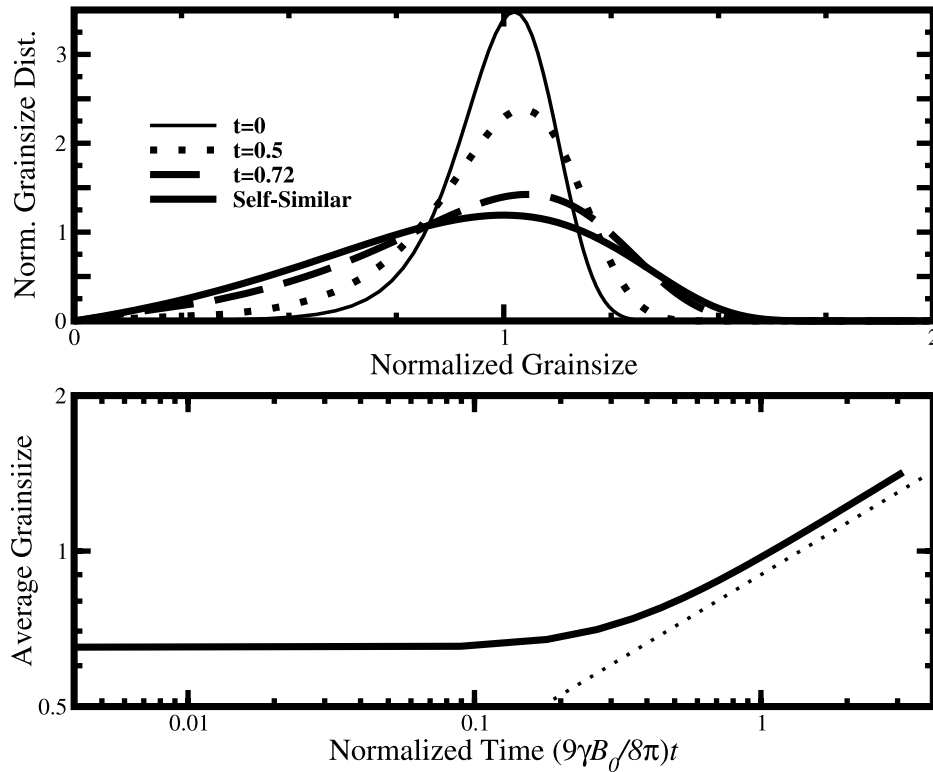
Figure 2. Evolution of the distribution of grain sizes with time in the coarsening case computed with a finite difference code with a second order of precision in time and second-order upwind in grain size. (top) Distribution (normalized so that its integral is constant) as a function of the normalized grain size $\mathcal{R}/\overline{\mathcal{R}}$. The arbitrarily chosen distribution at time $t = 0$ (a Gaussian in $\breve{m}$, thin curve) evolves with time toward the self-similar distribution given by H (thick solid curve). The other curves (dotted and dashed) correspond to intermediate normalized times. (bottom) The average grain size $\overline{\mathcal{R}}$ varies rapidly as $(9\gamma B_0^2 t/(8\pi))^{1/3}$, as predicted by the analytical solution (the dotted line has a slope of 1/3 in logarithmic axis.

Appendix A that (73c) and (86) have asymptotic self-similar solutions of the form

$$\mathcal{V}_\mathcal{R} = A(t)H(u) = A(t)H\left(\frac{\mathcal{R}}{\langle\mathcal{R}\rangle}\right), \qquad (88)$$

where H is the normalized shape of the grain size distribution, A its amplitude, and the average radius is found to vary as

$$\langle\mathcal{R}\rangle \propto t^{1/(7-2p)}. \qquad (89)$$

[81] Our definition of $\langle\mathcal{R}\rangle$ is chosen to simplify the analytic operations; but in the asymptotic self-similar regime $\overline{\mathcal{R}}$ and $\langle\mathcal{R}\rangle$ are proportional within a factor of order 1 (i.e., the inverse of the average radius is close and proportional to the average of the inverse radius). Experimentally, the average radius is often found to increase as $t^{1/3}$ which suggests that $p \approx 2$. With this value of p, the asymptotic self-similar distribution (see Appendix A) is

$$H(u) = \frac{u}{(2-u)^5}e^{(6/(u-2))} \quad \text{with} \quad \langle\mathcal{R}\rangle^3 = \langle\mathcal{R}_0\rangle^3 + \frac{9B_0^2\gamma}{8\Pi}t. \quad (90)$$

(where $\langle\mathcal{R}_0\rangle$ is $\langle\mathcal{R}\rangle$ when $t = 0$). The distribution and growth rate given above are in agreement with previous findings [*Lifshitz and Slyozov*, 1961; *Hillert*, 1965].

[82] However, the distribution has a self-similar shape when it initiates that way and will remain so during further evolution. To study the evolution of any arbitrary initial grain size distribution, one must solve (73c) and (86) numerically. For coarsening, the advection velocity in $\mathcal{R}$ space, $\dot{\mathcal{R}}$, points outward from the integration domain (i.e., $\dot{\mathcal{R}}$ is negative near $\mathcal{R} = 0$ where grains shrink, and positive for $\mathcal{R} \to +\infty$ where grains grow), thus one does not need to impose explicit boundary conditions (i.e., no information is coming from outside the domain).

[83] Figure 2 shows the evolution of an arbitrary distribution of grain size (assumed Gaussian in grain mass distribution) with time. The average radius (Figure 2, bottom) follows very closely the prediction of the analytical similarity solution even when the grain size distribution is far from its final self-similar shape. The grain size distributions at various normalized times, are depicted in Figure 2 (top) as a function of the normalized radius $\mathcal{R}/\langle\mathcal{R}\rangle$. The distributions are normalized so that their integrals (i.e., the number of grains per unit volume) are equal to a constant (arbitrarily set to 1). The distributions depicted at the normalized times 0, 0.5 and 0.72 are evolving toward the self-similar solution and become rapidly indistinguishable from it. Although the normalized distribution tends toward a time-independent solution in $u = \mathcal{R}/\langle\mathcal{R}\rangle$ space, in dimensional grain size space, the distribution moves toward

larger and less numerous grains (i.e., migrates right and collapses).

6. Static Grain Growth by Discontinuous Process

[84] We next consider static grain growth (i.e., with no damage, $\Psi = 0$) when grain populations change discontinuously by coalescence or breaking of grains of remote grain size populations, rather than by continuous exchange of mass between grains. Thus considering no continuous exchange ($\check{\mathcal{R}} = 0$), the positivity of entropy source (70) together with the conservation of mass and of grain size distribution, (27) and (20), leads to the system

$$-\int_0^\infty \frac{3}{2}\gamma\check{\mathcal{K}}\check{m}\Gamma_\mathcal{R}\,d\mathcal{R} \geq 0, \tag{91a}$$

$$\int_0^\infty \check{m}\Gamma_\mathcal{R}\,d\mathcal{R} = 0, \tag{91b}$$

$$\frac{\partial \mathcal{V}_\mathcal{R}}{\partial t} = \Gamma_\mathcal{R}. \tag{91c}$$

6.1. Source Terms $\Gamma_\mathcal{R}$ or $\Gamma_\mathcal{M}$

[85] The source terms $\Gamma_\mathcal{R}$ or $\Gamma_\mathcal{M}$ of the evolution equations, (16) and (20) are necessary to account for the fact that the number of grains can change by coalescence or fracturing. Nucleation can also be viewed as extracting a small subgrain from a larger one. Such processes of division and coalescence are well studied in the domains of polymer chemistry [*Stockmayer*, 1943], cellular biology [*Neelamegham et al.*, 1997], algae population growth [*Ackleh and Fitzpatrick*, 1997], planetary formation [*Wetherill*, 1990] and the general physics of aggregation [*Collet*, 2004]. The generalized formalism that we adopt from these studies is often called the Smoluchowski formalism [*von Smoluchowski*, 1917]. Since mass conservation is more easily expressed with mass distribution than it is with grain size distribution we focus on the source term $\Gamma_\mathcal{M}$, from which $\Gamma_\mathcal{R}$ can be readily deduced (see equation (21)).

[86] We first consider aggregation kinetics, in particular the coalescence of only two grains of masses $\check{m}'$ and $\check{m}''$ to form a new grain of mass $\check{m}' + \check{m}''$. The rate that a fraction of the number of grains of size $\check{m}''$ stick to the available grains of mass between $\check{m}'$ and $\check{m}' + d\check{m}'$ is given by $\Omega_+(\check{m}')d\check{m}'$. Thus the rate that all grains of size $\check{m}''$ stick to those of size $\check{m}'$ is given by $\Omega_+ d\check{m}'\mathcal{V}_\mathcal{M}(\check{m}'')d\check{m}''$. However, Ω_+ clearly depends on the number of available grains of mass $\check{m}'$ and thus $\Omega_+ = \Lambda_+\mathcal{V}_\mathcal{M}(\check{m}')$ where Λ_+ is a reaction rate. The rate of coalescence between these two populations of grains is therefore $\Lambda_+(\check{m}',\check{m}'')\mathcal{V}_\mathcal{M}(\check{m}')d\check{m}'\mathcal{V}_\mathcal{M}(\check{m}'')d\check{m}''$. Both this net rate and Λ_+ itself are necessarily symmetric in $\check{m}'$ and $\check{m}''$ (i.e., the rate that population 1 sticks to population 2 is the same as the rate that population 2 sticks to population 1); we also define Λ_+ to be positive (i.e., any reversal of sticking through breaking is treated by a separate quantity below).

[87] The effect of this aggregation reaction on a population of grains of mass $\check{m}$ is twofold. First, if $\check{m}$ is the resulting mass such that $\check{m} = \check{m}' + \check{m}''$ (or $\check{m}'' = \check{m} - \check{m}'$) then the population of grains of mass $\check{m}$ will increase at a rate $\Gamma_\mathcal{M}(\check{m})d\check{m}$ given by $\Lambda_+(\check{m}',\check{m}-\check{m}')\mathcal{V}_\mathcal{M}(\check{m}')\mathcal{V}_\mathcal{M}(\check{m}-\check{m}')d\check{m}'d\check{m}$ (note that $d\check{m}'' = d(\check{m}-\check{m}') = d\check{m}$ for a given, fixed $\check{m}'$). Second, if $\check{m}$ is the mass of the reacting population (i.e., coalescing with grains of mass $\check{m}'$) then $\check{m}'' = \check{m}$; in this case, the population of grains of mass $\check{m}$ will decrease at a rate $\Gamma_\mathcal{M}(\check{m})d\check{m}$ given by $-\Lambda_+(\check{m}',\check{m})\mathcal{V}_\mathcal{M}(\check{m}')\mathcal{V}_\mathcal{M}(\check{m})d\check{m}'d\check{m}$. This coalescence reaction is of course just for sticking to masses of particular size $\check{m}'$ and we must account for all possible masses by integrating over $\check{m}'$; but first we will consider the counterpart to coalescence, i.e., breaking.

[88] For fracturing of grains we consider the rate that a fraction of the number of grains of an original mass $\check{m}^*$ break into grains of sizes $\check{m}'$ and $\check{m}''$ where of course $\check{m}^* = \check{m}' + \check{m}''$; we write this fractional rate as $\Omega_-\,d\check{m}'$ to denote that the fracturing will create grains in the interval between $\check{m}'$ and $\check{m}' + d\check{m}'$ (as well as the complementary interval around the size $\check{m}'' = \check{m}^* - \check{m}'$, although this is already constrained by knowing $\check{m}'$). The net rate that the population of grains of mass $\check{m}^*$ will break is therefore $\Omega_-\,d\check{m}'\mathcal{V}_\mathcal{M}(\check{m}^*)d\check{m}^*$. Unlike the case for coalescence we do not expect Ω_- to depend on either of the product populations $\mathcal{V}_\mathcal{M}(\check{m}')$ and $\mathcal{V}_\mathcal{M}(\check{m}'')$ (since either could be 0 and still breaking should occur), but it will depend on the resulting masses symmetrically, such that $\Omega_- = \Lambda_-(\check{m}',\check{m}'')$, where Λ_- is a positive and symmetric function. As with coalescence, breaking can affect the population of grains of mass $\check{m}$ in two ways. First, if grains of mass $\check{m}$ undergo fracturing then $\check{m}^* = \check{m}$ and the rate of change of their population $\Gamma_\mathcal{M}(\check{m})d\check{m}$ is negative (i.e., there is loss of these grains) and is given by $-\Lambda_-(\check{m}',\check{m}-\check{m}')d\check{m}'\mathcal{V}_\mathcal{M}(\check{m})d\check{m}$. Second, if the grains of mass $\check{m}$ are produced by fracturing (i.e., $\check{m}$ is one of the product masses) then $\check{m}'' = \check{m}$ and $\check{m}^* = \check{m}' + \check{m}$, in which case the rate of change of this population $\Gamma_\mathcal{M}(\check{m})d\check{m}$ is positive (since these grains are being produced) and is given by $+\Lambda_-(\check{m}',\check{m})d\check{m}'\mathcal{V}_\mathcal{M}(\check{m}+\check{m}')d\check{m}$ (where, again, in this case $d\check{m}^* = d\check{m}$).

[89] Combining the rates given by both aggregation and fracturing and integrating over all possible reacting or product masses $\check{m}'$, we obtain

$$\Gamma_\mathcal{M}(\check{m}) = \frac{1}{2}\int_0^\infty \Lambda_+(\check{m}',\check{m}-\check{m}')\mathcal{V}_\mathcal{M}(\check{m}')\mathcal{V}_\mathcal{M}(\check{m}-\check{m}')d\check{m}'$$

$$-\int_0^\infty \Lambda_+(\check{m}',\check{m})\mathcal{V}_\mathcal{M}(\check{m}')\mathcal{V}_\mathcal{M}(\check{m})d\check{m}'$$

$$+\int_0^\infty \Lambda_-(\check{m}',\check{m})\mathcal{V}_\mathcal{M}(\check{m}+\check{m}')d\check{m}'$$

$$-\frac{1}{2}\int_0^\infty \Lambda_-(\check{m}',\check{m}-\check{m}')\mathcal{V}_\mathcal{M}(\check{m})d\check{m}', \tag{92}$$

where the factor $1/2$ is necessary to avoid counting interacting distributions of grains twice (i.e., while integrating in $\check{m}'$ we encounter at small $\check{m}'$, interaction of grains of mass $\check{m}' = \check{m}_0$ and $\check{m} - \check{m}_0$, and later, at larger $\check{m}'$, we encounter interaction of grains of mass $\check{m}' = \check{m} - \check{m}_0$ and $\check{m}_0$). We choose by convention to have $\Lambda_+(x,y) = \Lambda_-(x,y) = 0$ if either argument x or y is negative, hence all integrals involving $\check{m} - \check{m}'$, and for which $0 < \check{m}' < \check{m}$, can be extended to $0 < \check{m}' < \infty$.

[90] A symmetrical relation for $\Gamma_\mathcal{M}$ can also be derived [e.g., *Leyvraz*, 2003],

$$\Gamma_\mathcal{M}(\check{m}) = \frac{1}{2}\iint_0^\infty E(\check{m}',\check{m}'')\Delta(\check{m},\check{m}',\check{m}'')d\check{m}'d\check{m}'', \tag{93}$$

where, for the two variables $\check{m}'$ and $\check{m}''$, the integrations are from 0 to ∞, and where

$$
\begin{aligned}
E(\check{m}', \check{m}'') &= \Lambda_+(\check{m}', \check{m}'') \mathcal{V}_{\mathcal{M}}(\check{m}') \mathcal{V}_{\mathcal{M}}(\check{m}'') \\
&\quad - \Lambda_-(\check{m}', \check{m}'') \mathcal{V}_{\mathcal{M}}(\check{m}' + \check{m}''), \Delta(\check{m}, \check{m}', \check{m}'') \\
&= \delta(\check{m} - \check{m}' - \check{m}'') - \delta(\check{m} - \check{m}') - \delta(\check{m} - \check{m}''), \quad (94)
\end{aligned}
$$

where δ is the Dirac function. The function E is a reaction rate and the equilibrium equation $E = 0$ suggests a relation between grain populations of different sizes, analogous to the usual law of mass action for chemical reactions

$$
\frac{\mathcal{V}_{\mathcal{M}}(\check{m}') \mathcal{V}_{\mathcal{M}}(\check{m}'')}{\mathcal{V}_{\mathcal{M}}(\check{m}' + \check{m}'')} = \frac{\Lambda_-(\check{m}', \check{m}'')}{\Lambda_+(\check{m}', \check{m}'')}. \quad (95)
$$

One can easily verify that mass conservation, (27), is automatically satisfied since

$$
\begin{aligned}
\int_0^\infty \check{m} \Gamma_{\mathcal{M}}(\check{m}) d\check{m} &= \frac{1}{2} \iint_0^\infty E(\check{m}', \check{m}'') \\
&\quad \cdot \left(\int_0^\infty \check{m} \Delta(\check{m}, \check{m}', \check{m}'') d\check{m} \right) d\check{m}' d\check{m}'' \\
&= \frac{1}{2} \iint_0^\infty E(\check{m}', \check{m}'') \\
&\quad \cdot \left((\check{m}' + \check{m}'') - \check{m}' - \check{m}'' \right) d\check{m}' d\check{m}'' = 0. \quad (96)
\end{aligned}
$$

6.2. Static Grain Evolution (No Damage)

[91] We can replace the relation for $\Gamma_{\mathcal{M}}$, (93), in the expression for the entropy sources (69). The term $-(3/2)\gamma\check{K}\check{m}$ is also $-\gamma(36\Pi\rho)^{1/3}\check{m}^{2/3}$, and since $\Gamma_{\mathcal{R}} d\mathcal{R} = \Gamma_{\mathcal{M}} d\check{m}$, we obtain

$$
\begin{aligned}
-\int_0^\infty \frac{3}{2} \gamma \check{K} \check{m} \Gamma_{\mathcal{M}} d\check{m} &= \gamma \left(\frac{9\Pi\rho}{2} \right)^{1/3} \\
&\quad \times \iint_0^\infty E(\check{m}', \check{m}'') \left(\int_0^\infty -\check{m}^{2/3} \Delta(\check{m}, \check{m}', \check{m}'') d\check{m} \right) d\check{m}' d\check{m}'' \\
&= \gamma \iint_0^\infty E(\check{m}', \check{m}'') \mathcal{A}(\check{m}', \check{m}'') d\check{m}' d\check{m}'' \geq 0, \quad (97)
\end{aligned}
$$

where

$$
\mathcal{A}(\check{m}', \check{m}'') = \left(\frac{9\Pi\rho}{2} \right)^{1/3} \left(\check{m}'^{2/3} + \check{m}''^{2/3} - (\check{m}' + \check{m}'')^{2/3} \right). \quad (98)
$$

is related to the change in surface area during grain sticking or fracturing and has units kg m^{-1}. This function is strictly positive unless $\check{m}' = \check{m}'' = 0$. Therefore, in the case of no deformation ($\Psi = 0$), the positivity of entropy production is guaranteed for any distribution of grain mass if $E(\check{m}', \check{m}'') \geq 0$. From the definition of E (see (94)) entropy production is only guaranteed positive for any distribution if the rate of grain breaking Λ_- is zero (this conclusion assumes that the rates Λ_- and Λ_+ are only functions of the grain masses $\check{m}$ and $\check{m}'$, and not of the grain size distributions themselves). Otherwise in the limit where the grain number tends to 1, the remaining grain

could still possibly break, but there would be no other grain to coalesce with, and this could violate the second law of thermodynamics by causing $E < 0$. Without damage, the possibility of two grains sticking is allowed by the second law of thermodynamics, but $\Lambda_- = 0$ implies no possibility for any grain to break.

[92] Therefore, in the case of no damage, the general evolution of grain distribution must verify

$$
\frac{d\mathcal{V}_{\mathcal{M}}(\check{m})}{dt} = \frac{1}{2} \iint_0^\infty \Lambda_+(\check{m}', \check{m}'') \Delta(\check{m}, \check{m}', \check{m}'') dn' dn'', \quad (99)
$$

where dn' and dn'' stand for $\mathcal{V}_{\mathcal{M}}(\check{m}') d\check{m}'$ and $\mathcal{V}_{\mathcal{M}}(\check{m}'') d\check{m}''$. The kinetic rate Λ_+ is a positive function that might be deduced either experimentally or from a microscopic model. The rules of nonequilibrium thermodynamics suggest from (97) a phenomenological law between the reaction rate Λ_+ and the thermodynamic "force" $\gamma \mathcal{A}$ of the form

$$
\begin{aligned}
\Lambda_+(\check{m}', \check{m}'') &= \gamma \iint_0^\infty G^d(\check{m}', \check{m}'', \check{m}''', \check{m}'''') \\
&\quad \cdot \mathcal{A}(\check{m}''', \check{m}'''') dn''' dn'''', \quad (100)
\end{aligned}
$$

where $G^d(\check{m}', \check{m}'', \check{m}''', \check{m}'''')$ is another interaction function for the discontinuous sticking process. Equation (100) indicates that the chemical potential difference (stored as surface energy on the grains) before and after coalescence acts as a thermodynamic force that will drive the coalescence reaction, which is itself a form of "thermodynamic flux". The entropy production, according to (97), can be written

$$
\begin{aligned}
-\int_0^\infty \frac{3}{2} \gamma \check{K} \check{m} \Gamma_{\mathcal{M}} d\check{m} &= \gamma^2 \iiiint_0^\infty G^d(\check{m}', \check{m}'', \check{m}''', \check{m}'''') \\
&\quad \times \mathcal{A}(\check{m}', \check{m}'') \mathcal{A}(\check{m}''', \check{m}'''') dn' dn'' dn''' dn'''' \geq 0, \quad (101)
\end{aligned}
$$

which is positive provided G^d is itself a positive definite operator. The operator G^d should be invariant to the permutation of its four variables since $\Lambda_+(\check{m}', \check{m}'')$ is invariant to a permutation of $\check{m}'$ and $\check{m}''$, and $G^d(\check{m}', \check{m}'', \check{m}''', \check{m}'''')$ is invariant to a permutation of $(\check{m}', \check{m}'')$ with $(\check{m}''', \check{m}'''')$ by Onsager's symmetry rules (i.e., the cross-coupling coefficients that relate the 'flux' $\Lambda_+(\check{m}', \check{m}'')$ to the 'force' $\gamma \mathcal{A}(\check{m}''', \check{m}'''')$ are symmetric with the cross-coupling coefficients relating the 'flux' $\Lambda_+(\check{m}''', \check{m}'''')$ to the 'force' $\gamma \mathcal{A}(\check{m}', \check{m}'')$).

6.3. Example of Grain Coalescence

[93] A few cases of exact solutions for aggregation kinetics are known [*Leyvraz*, 2003; *Collet*, 2004] and the continuous representation is often replaced by a discrete set of equations where "monomers" (the smallest "grain size") can be successively added to larger clusters as in the seminal paper of *Becker and Doring* [1935]. As an example, we assume here that the sticking rate, often called the aggregation kernel in the mathematical literature [e.g., *Collet*, 2004], is a constant rate $\Lambda_+(\check{m}', \check{m}'') = C_0 \gamma$, regardless of the masses, $\check{m}'$ and $\check{m}''$, of the grains that stick together. This is clearly a very simplified view of the generic phenomenological equation (100) but for which an analytical solution is possible. In this case, the integra-

tion of (99), taking into accounting the Dirac functions of Δ, leads to

$$\frac{d\mathcal{V}_\mathcal{M}(\check{m})}{dt} = C_0\gamma\left(\frac{1}{2}\int_0^m \mathcal{V}_\mathcal{M}(\check{m}')\mathcal{V}_\mathcal{M}(\check{m}-\check{m}')d\check{m}' \right.$$
$$\left. - \mathcal{V}_\mathcal{M}(\check{m})\int_0^\infty \mathcal{V}_\mathcal{M}(\check{m}')d\check{m}'\right). \tag{102}$$

[94] This first integral is computed up to $\check{m}' = \check{m}$ only, since only grains smaller than $\check{m}$ can coalesce to produce a grain of mass $\check{m}$.

[95] Here again, self-similar solutions can be found (see Appendix B) by assuming $\mathcal{V}_\mathcal{M}(\check{m}) = A(t)H(\check{m}/\overline{m})$ where $\overline{m} = \int \mathcal{V}_\mathcal{M}\check{m}d\check{m}/\int \mathcal{V}_\mathcal{M}d\check{m}$ (i.e., choosing $B(\check{m}) = 1$ in (84)). The average mass is found to satisfy

$$\overline{m} = \overline{m}_0 + \frac{1}{2}\rho C_0\gamma t, \tag{103}$$

(with $\overline{m}_0 = \overline{m}$ ($t = 0$)) and the asymptotic mass size distribution

$$\mathcal{V}_\mathcal{M}(\check{m},t) = \frac{\rho}{\overline{m}^2}\exp\left(-\frac{\check{m}}{\overline{m}}\right), \tag{104}$$

and since $\mathcal{V}_\mathcal{R} = 4\pi\mathcal{R}^2\rho\mathcal{V}_\mathcal{M}$ according to (8), the asymptotic grain size distribution would be

$$\mathcal{V}_\mathcal{R} \propto u^2\exp(-u^3), \tag{105}$$

where $u = \mathcal{R}/\langle\mathcal{R}\rangle$ and $\langle\mathcal{R}\rangle \sim \overline{m}^{1/3}$.

[96] The existence of a self-similar solution, depends on the behavior of Λ_+. When $\Lambda_+(\check{m}',\check{m}'')$ increases faster than the product $\check{m}'\check{m}''$, a "gelation" can occur where the largest grain size diverges (reaches an infinite size) in a finite time [*Leyvraz*, 2003]. However, in our theory, even when the interaction function G^d is a constant, the reaction rate $\Lambda_+(\check{m}',\check{m}'')$ is related to the 2 / 3 power of $\check{m}'$ and $\check{m}''$ (see (98) and (100)) and should still yield self-similar solutions.

[97] As with the coarsening case, we study numerically (using the same approach as in section 5.2), the evolution of a test case distribution of grain size with time for the assumed reaction rate $\Lambda_+ = \gamma C_0$ (see Figure 3). The average radius (Figure 3, bottom) follows very closely the prediction of the analytical solution. The normalized grain size distribution (normalized so that the integral of the distribution is 1) is depicted in the Figure 3 (top) as a function of the normalized radius $(\check{m}/\overline{m})^{1/3}$ (the average radius used in Figure 2 and the radius of the average mass are proportional by a factor $\mathcal{O}$ (1)). The normalized distributions shown at the dimensionless times 0, 0.5 and 0.72 evolve toward the self-similar solution. The distributions appear to spread toward smaller grains; however, this is due to the fact that they are plotted with respect to normalized sizes. The normalized distributions as a function of the real grain sizes (see Figure 3, middle) show on the contrary, that the number of grains with a small size simply decreases while new and larger grains are created (i.e., the grain size distribution changes by only expanding its right tail, which leads to a twice slower shift of the average grain size toward larger

sizes). The average grain mass is increasing linearly with time as plotted in Figure 3 (bottom).

6.4. Coupled Continuous and Discontinuous Processes: Static Grain Growth and Coalescence

[98] The equations that we have obtained for the continuous mass transfer (78) and discontinuous reaction rate (100) may not be the most general even in the static case (i.e., in the absence of deformational work). The continuous and discontinuous processes are potentially coupled according to

$$\frac{d\check{m}}{dt} = \gamma\int_0^\infty G^c(\check{m},\check{m}')\left(\check{\mathcal{K}}'-\check{\mathcal{K}}\right)dn'$$
$$+ \gamma\iint_0^\infty G^{cd}(\check{m},\check{m}',\check{m}'')\mathcal{A}(\check{m}',\check{m}'')dn'dn'' \tag{106a}$$

$$\Lambda_+(\check{m},\check{m}') = \gamma\int_0^\infty G^{dc}(\check{m}'',\check{m}',\check{m})\check{\mathcal{K}}''dn''$$
$$+ \gamma\iint_0^\infty G^d(\check{m},\check{m}',\check{m}'',\check{m}''')\mathcal{A}(\check{m}'',\check{m}''')dn''dn''', \tag{106b}$$

(where, for consistency, we treat all variables as functions of grain masses since integration can be done either with respect to grain size or grain mass using the fact that $dn = \mathcal{V}_\mathcal{R}d\mathcal{R} = \mathcal{V}_\mathcal{M}d\check{m}$).

[99] Coupling between continuous and discontinuous processes conceivably exists through the coefficients G^{cd} and G^{dc}. $G^{cd}(\check{m},\check{m}',\check{m}'')$ represents the influence on the diffusive growth rate of grains of mass $\check{m}$ due to the presence of (i.e., chemical potentials of) grains of masses $\check{m}'$ and $\check{m}''$. Reciprocally, $G^{dc}(\check{m}'',\check{m}',\check{m})$ is the influence on the aggregation rate between grains of masses $\check{m}$ and $\check{m}'$ due to the presence of grains of size $\check{m}''$.

[100] Onsager's reciprocal relations between the arguments of G^{dc} and G^{cd} can be inferred by considering the contribution to the entropy production by these cross-terms (using (70) with (97) and the intrinsic symmetry of $\mathcal{A}$ given by (98))

$$\dot{S}_{\text{cross}} = -\gamma^2\iiint_0^\infty \check{\mathcal{K}}\mathcal{A}(\check{m}',\check{m}'')$$
$$\times\left[G^{cd}(\check{m},\check{m}',\check{m}'')-G^{dc}(\check{m},\check{m}',\check{m}'')\right]dndn'dn'' \tag{107}$$

The positivity of entropy is best guaranteed by Onsager's symmetry relationship $G^{dc}(\check{m},\check{m}',\check{m}'') = G^{cd}(\check{m},\check{m}',\check{m}'')$, which states that the law governing how the aggregation of two grains is influenced by the diffusive growth of a third grain is the same as that which governs how diffusive growth of the third grain is influenced by the two aggregating grains.

[101] However, we have assumed that mass conservation is separately satisfied by the continuous and the discontinuous processes. Since the term containing G^c in (106a) already satisfies mass conservation, then the term containing G^{cd} must by itself satisfy mass conservation. Since $\mathcal{A}(\check{m}',\check{m}'')$ is a symmetric function, the best guarantee that mass is conserved is for the function G^{cd} to be antisymmetric in $\check{m}'$ and $\check{m}''$ so that $G^{cd}(\check{m},\check{m}',\check{m}'') = -G^{cd}(\check{m},\check{m}'',\check{m}')$.
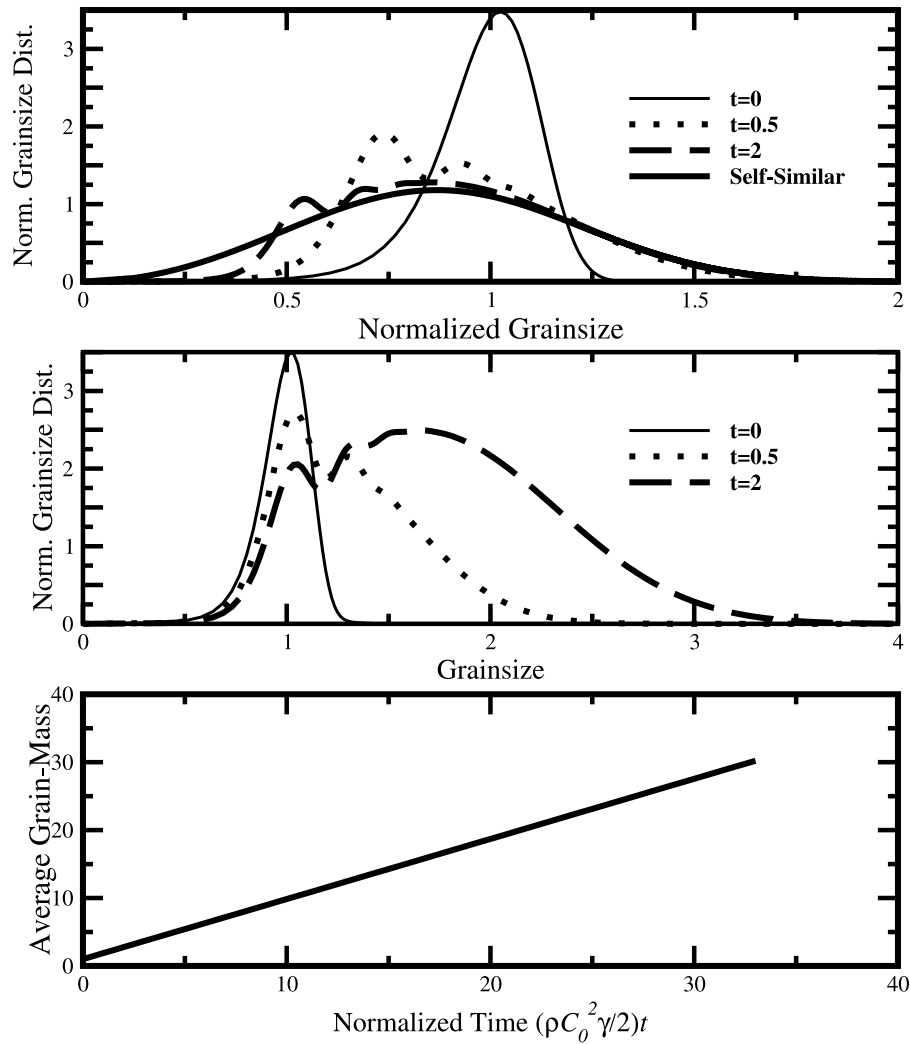
Figure 3. Same as in Figure 2, evolution of the distribution of grain sizes with time, when grain can stick together. (top) Normalized distribution as a function of the normalized grain size $\mathcal{R}/\overline{\mathcal{R}}$. The arbitrarily chosen distribution at time $t = 0$ (a Gaussian in $\check{m}$, thin curve) evolves with time toward the self-similar distribution (thick solid curve). The other curves (dotted and dashed) correspond to intermediate normalized times. (middle) Although the normalized distribution tends toward a time-independent solution, in unnormalized grain size space, the distribution moves toward larger grains; this shows normalized distribution amplitudes because the peak of the beginning distribution ($t = 0$) is more than an order or magnitude greater and that of the final one ($t = 2$). (bottom) The average grain mass $\overline{m}$ varies rapidly as $(\rho\gamma C_0{}^2/2)\,t$ as predicted by the analytical solution.

Onsager's relations then imply that G^{dc} is also antisymmetric with respect to its last two variables: $G^{dc}(\check{m}'', \check{m}', \check{m}) = -G^{dc}(\check{m}'', \check{m}, \check{m}')$. This is however impossible as $\Lambda_+(\check{m}, \check{m}')$ in (106b) is itself a symmetric function. Therefore the only possible solution is that G^{dc}, and thus G^{cd} are both zero. This analysis implies that the phenomenological laws governing continuous coarsening and discontinuous coalescence are decoupled with regard to continuous and discontinuous thermodynamics forces and fluxes; however, some coupling exists regardless since the forces $\gamma\check{\mathcal{K}}$ and $\gamma\mathcal{A}$ both depend on grain size.

7. Grain Size Evolution With Damage

[102] A major goal of this study is to go beyond simple static grain growth by either coarsening or coalescence and to treat nonstatic cases that include deformation and damage. As with static grain growth, the general phenomenological grain size law is inferred by satisfying positivity of entropy production stipulated in (70) [e.g., *de Groot and Mazur*, 1984]. Entropy production associated with deformational work for irrecoverable deformation Ψ is already known to be positive definite. (Note that if the medium were viscoelastic then the elastic component of Ψ would only make a contribution to the reversible internal energy, akin to the $-PdV$ term [*Malvern*, 1969], and the remaining viscous part would be a positive definite entropy source.)

[103] Although positivity of entropy production is best guaranteed by positive definiteness of individual entropy sources, this is not the most general statement of the 2nd law of thermodynamics. Entropy can of course be exchanged between coupled processes and all the 2nd law really

requires is that the net entropy production be positive. Thus we now discuss the possible coupling between the different entropy sources.

[104] One of the basic hypotheses of damage mechanics is that a portion of deformational work is stored as a free energy on defects in the continuum (cracks, voids, dislocations, grain boundaries) rather than as dissipative heating [*Ashby and Sammis*, 1990; *Hansen and Schreyer*, 1992; *Lemaitre*, 1992; *Krajcinovic*, 1996; *Lyakhovsky et al.*, 1997; *Bercovici et al.*, 2001a; *Bercovici and Ricard*, 2003; *Ricard and Bercovici*, 2003; *Austin and Evans*, 2007]; in the case of grain growth it is manifest as increasing grain boundary surface energy by making more smaller grains and thus reducing the mean grain size. This effect can be stated in two equivalent ways: Either (1) some portion of deformational work is used to create stored energy, and thus does not go into entropy production; or (2) the storage of free energy provides an entropy sink (see for example section 6.2 in which entropy production associated with the grain breaking rate Λ_- is negative), which is necessarily offset, to preclude violation of the 2nd law of thermodynamics, by some portion of mechanical dissipation (i.e., deformational work). In either description, a portion of a given entropy source (deformational work) is used to balance a nonentropic process (grain size reduction).

[105] The total entropy production during grain evolution in the presence of deformation is given by (70), which we write as having the standard positive definite contributions from grain growth (coarsening and coalescence) and deformational work, but where a fraction $\breve{f}$ of the deformational work is not used for entropy production (i.e., it is used for surface energy creation instead of heating):

$$\int_0^\infty \left(-\gamma \breve{\mathcal{K}} \frac{d\breve{m}}{dt} \mathcal{V}_\mathcal{R}(\mathcal{R}) - \frac{3}{2} \gamma \breve{\mathcal{K}} \breve{m} \Gamma_\mathcal{R} + \breve{m} \Psi \mathcal{V}_\mathcal{R}(\mathcal{R}) \right) d\mathcal{R} =$$
$$+ \frac{\gamma^2}{2} \iint_0^\infty G^c(\mathcal{R}, \mathcal{R}') \left(\breve{\mathcal{K}}' - \breve{\mathcal{K}} \right)^2 dn dn'$$
$$+ \gamma^2 \iiiint_0^\infty G^d(\breve{m}, \breve{m}', \breve{m}'', \breve{m}''')$$
$$\times \mathcal{A}(\breve{m}, \breve{m}') \mathcal{A}(\breve{m}'', \breve{m}''') dn dn' dn'' dn'''$$
$$+ \int_0^\infty \left(1 - \breve{f}(\mathcal{R}) \right) \breve{m} \Psi \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R} \geq 0, \tag{108}$$

where G^c, G^d, and $\mathcal{A}$ are the same grain functions described in section 5; we have also used the identity $\rho \Psi = \int_0^\infty \breve{m} \Psi \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R}$, and employed the results of section 6.4 (i.e., $G^{cd} = G^{dc} = 0$). The factor $\breve{f}(\mathcal{R})$ is a work-partitioning function that indicates how much deformational work is used to create surface energy and which therefore does not immediately cause dissipative heating (and hence represents a small nonpositive contribution to entropy production). Therefore implicit in (108) is that the grain evolution processes represented by the first two terms in the integral on the left of the equation include not only positive-definite entropy sources (the first two terms on the right side) but also nonentropic, or conservative, components (i.e., surface energy storage by grain reduction) that are offset by a fraction of the deformational work $\breve{f} \Psi$. The

nonentropic damage processes are thus constrained by (simply rearranging (108))

$$\int_0^\infty \left(-\gamma \breve{\mathcal{K}} \frac{d\breve{m}}{dt} \mathcal{V}_\mathcal{R}(\mathcal{R}) - \frac{3}{2} \gamma \breve{\mathcal{K}} \breve{m} \Gamma_\mathcal{R} \right) d\mathcal{R}$$
$$- \frac{\gamma^2}{2} \iint_0^\infty G^c(\mathcal{R}, \mathcal{R}') \left(\breve{\mathcal{K}}' - \breve{\mathcal{K}} \right)^2 dn dn'$$
$$- \gamma^2 \iiiint_0^\infty G^d(\breve{m}, \breve{m}', \breve{m}'', \breve{m}''')$$
$$\times \mathcal{A}(\breve{m}, \breve{m}') \mathcal{A}(\breve{m}'', \breve{m}''') dn dn' dn'' dn'''$$
$$= - \int_0^\infty \breve{f}(\mathcal{R}) \breve{m} \Psi \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R}. \tag{109}$$

[106] The partitioning function $\breve{f}(\mathcal{R})$ also potentially contains information about the rheological grain size dependence and distribution, i.e., how, and even if, viscosity depends on grain size. This can be seen by considering an alternative and seemingly more general form of the last term on the right side of (109) in which we could have employed $\breve{\Psi}(\mathcal{R})$, the deformational work on grains of size $\mathcal{R}$, rather than the average, grain-size-independent work Ψ; in this case the term in question would have been $\int_0^\infty \tilde{f}(\mathcal{R}) \breve{m} \breve{\Psi} \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R}$ where $\tilde{f}$ is an alternative work-partitioning function. As we consider velocity independent of grain size, then $\breve{\Psi}$ only depends on grain size through grain viscosity $\breve{\eta}(\mathcal{R})$ and thus we can write $\breve{\Psi}(\mathcal{R}) = (\breve{\eta}(\mathcal{R})/\eta) \Psi$ where η is the volume-averaged viscosity (see for example (44)). The revised last term of (109) would thus become $\int_0^\infty \tilde{f}(\mathcal{R}) [\breve{\eta}(\mathcal{R})/\eta] \breve{m} \Psi \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R}$ which simply means we can define $\breve{f}(\mathcal{R}) = \tilde{f}(\mathcal{R}) \breve{\eta}(\mathcal{R})/\eta$ and recover (109), identically. Therefore, although we have shown that the form of this term in (109) is general as is, we have also demonstrated that the work-partitioning function is conceivably and quite plausibly a function of the grain size dependence of viscosity. This has significance toward the functionality of dynamic recrystallization as is discussed below in section 9.

[107] The net viscous dissipation, $\int_0^\infty \left(1 - \breve{f}(\mathcal{R}) \right) \breve{m} \Psi \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R}$, cannot be negative and cannot exceed the available deformational work ($\rho \Psi$ in (70)), therefore,

$$0 \leq \Psi \int_0^\infty \left[1 - \breve{f}(\mathcal{R}) \right] \breve{m} \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R} \leq \rho \Psi \tag{110}$$

leading to

$$0 \leq f = \int_0^\infty \breve{f}(\mathcal{R}) \breve{v} \mathcal{V}_\mathcal{R}(\mathcal{R}) d\mathcal{R} \leq 1, \tag{111}$$

where f is the average proportion of viscous dissipation removed from the entropy sources that is converted into surface energy.

[108] The term $\breve{f}$ and its macroscopic average f are the sum of continuous and discontinuous processes and can be written as $\breve{f} = \breve{f}_c + \breve{f}_d$ and $0 \leq f = f_c + f_d \leq 1$. We therefore divide (109) into

$$\int_0^\infty \left(-\gamma \breve{\mathcal{K}} \frac{d\breve{m}}{dt} \mathcal{V}_\mathcal{R}(\mathcal{R}) \right) d\mathcal{R}$$
$$= \frac{\gamma^2}{2} \iint_0^\infty G^c(\mathcal{R}, \mathcal{R}') \left(\breve{\mathcal{K}}' - \breve{\mathcal{K}} \right)^2 dn dn'$$
$$- \int_0^\infty \breve{f}_c(\mathcal{R}) \breve{m} \Psi \mathcal{V}_\mathcal{R} d\mathcal{R} \geq 0, \tag{112}$$

and,

$$\int_0^\infty \left(\frac{3}{2} \gamma \check{\mathcal{K}} \check{m} \Gamma_{\mathcal{M}} \right) = \gamma^2 \iint_0^\infty G^d(\check{m}, \check{m}', \check{m}'', \check{m}''')$$
$$\times \mathcal{A}(\check{m}, \check{m}') \mathcal{A}(\check{m}'', \check{m}''') dn dn' dn'' dn'''$$
$$- \int_0^\infty \check{f}_d(\check{m}) \check{m} \Psi \mathcal{V}_{\mathcal{M}} d\check{m} \geq 0. \tag{113}$$

Here again, as in section 5.1 and section 6.1, we prefer to use grain size for the continuous process and grain mass for the discontinuous process.

7.1. Continuous Processes With Damage

[109] Assuming $\check{f}_d = 0$, and considering the possible coupling between grain growth and deformational work, the relevant system of equations (entropy positivity, mass and grain size distribution conservation, with $\check{f}_c \neq 0$ and $\check{f}_d = 0$ and $\Gamma_{\mathcal{R}} = 0$) becomes

$$\int_0^\infty \left[-\gamma \check{\mathcal{K}} \frac{d\check{m}}{dt} + \check{f}_c(\mathcal{R}) \Psi \check{m} \right] \mathcal{V}_{\mathcal{R}} d\mathcal{R}$$
$$= \frac{\gamma^2}{2} \iint_0^\infty G^c(\mathcal{R}, \mathcal{R}') \left(\check{\mathcal{K}}' - \check{\mathcal{K}} \right)^2 dn dn' \geq 0, \tag{114a}$$

$$\int_0^\infty \frac{d\check{m}}{dt} \mathcal{V}_{\mathcal{R}} d\mathcal{R} = 0, \tag{114b}$$

$$\frac{\partial \mathcal{V}_{\mathcal{R}}}{\partial t} + \frac{\partial (\dot{\mathcal{R}} \mathcal{V}_{\mathcal{R}})}{\partial \mathcal{R}} = 0. \tag{114c}$$

[110] The phenomenological grain growth relation required by (114a), and similar to (78), is

$$\frac{d\check{m}(\mathcal{R})}{dt} = \int_0^\infty G^c(\mathcal{R}, \mathcal{R}') \gamma \left[\check{\mathcal{K}}(\mathcal{R}') - \check{\mathcal{K}}(\mathcal{R}) \right] \mathcal{V}_{\mathcal{R}}(\mathcal{R}') d\mathcal{R}'$$
$$+ \frac{\check{f}_c(\mathcal{R}) \check{m}(\mathcal{R})}{\gamma \check{\mathcal{K}}(\mathcal{R})} \Psi \tag{115}$$

[111] The damage/deformational work term (last on the right side) in (115) is in fact quite general; a seemingly more general approach would have been to, as with the coarsening effect, construct this term as a convolution of work-partitioning contributions to all grains, which would have lead to a term of the form $\Psi \int_0^\infty H(\mathcal{R}, \mathcal{R}') \check{f}_c(\mathcal{R}') \check{m}(\mathcal{R}') \mathcal{V}_{\mathcal{R}}(\mathcal{R}') d\mathcal{R}'$ where $H(\mathcal{R}, \mathcal{R}')$ is a convolution or interaction function similar to $G^c(\mathcal{R}, \mathcal{R}')$. This term is, after integration in $\mathcal{R}'$ necessarily of the form $\Psi \mathcal{Z}(\mathcal{R})$ where $\mathcal{Z}(\mathcal{R})$ is simply the integral factor in that term; however, with this alternative term in (115), (114a) can only be satisfied if $\mathcal{Z}(\mathcal{R}) = \check{f}_c(\mathcal{R}) \check{m}(\mathcal{R}) / \gamma \check{\mathcal{K}}(\mathcal{R})$, which simply leads back to (115) in its original form.

[112] Finally, using the form of $G^c(\mathcal{R}, \mathcal{R}')$ assumed in (82), we obtain, as with (82),

$$\frac{d\check{m}(\mathcal{R})}{dt} = \gamma \beta(\mathcal{R}) \left[\overline{\mathcal{K}} - \check{\mathcal{K}}(\mathcal{R}) \right] + \frac{\check{f}_c(\mathcal{R}) \check{m}(\mathcal{R})}{\gamma \check{\mathcal{K}}(\mathcal{R})} \Psi \tag{116}$$

where $\beta(\mathcal{R})$ is given by (83) and $\overline{\mathcal{K}}$ is defined as in (84). Equation (116) manifests both coarsening under the influence of surface tension, as well as changes in grain size due to energy input from deformational work. However, just as with the grain interaction function $G^c(\mathcal{R}, \mathcal{R}')$, the work partitioning $\check{f}_c(\mathcal{R})$ must be elaborated on subject to various constraints such as mass conservation, as well as the second law of thermodynamics as given by (111).

7.1.1. Work Partitioning and the Damage Distribution

[113] To satisfy mass conservation (114b), the partitioning function $\check{f}_c(\mathcal{R})$ cannot have the same sign for all grain sizes (not all grains can simultaneous grow or shrink). The most general expression that satisfies mass conservation, is to require $\check{f}_c(\mathcal{R})$ to have the form of

$$\check{f}_c(\mathcal{R}) = \frac{\check{\mathcal{K}}}{\check{v}} \beta(\mathcal{R}) \left[\overline{\mathcal{H}} - \check{\mathcal{H}}(\mathcal{R}) \right], \tag{117}$$

where $\check{\mathcal{H}}(\mathcal{R})$ is an arbitrary function of $\mathcal{R}$, $\overline{\mathcal{H}}$ is defined as in (84), and recall that $\check{v} = \check{m}/\rho$. We assume that $\check{\mathcal{H}}(\mathcal{R})$ is monotonic in $\mathcal{R}$, i.e., grains are either more or less susceptible to damage as they get larger or smaller, but there are no extrema in which grains could reach a minimum or maximum damage susceptibility at a given size. Using (117) the grain growth law (76) now becomes

$$\frac{d\check{m}}{dt} = \beta(\mathcal{R}) \left(\gamma \left[\overline{\mathcal{K}} - \check{\mathcal{K}}(\mathcal{R}) \right] + \frac{\rho \Psi}{\gamma} \left[\overline{\mathcal{H}} - \check{\mathcal{H}}(\mathcal{R}) \right] \right). \tag{118}$$

[114] Whether $\check{\mathcal{H}}(\mathcal{R})$ increases or decreases with $\mathcal{R}$, determines the nature of the damage distribution, i.e., whether larger grains shrink (if $d\check{\mathcal{H}}(\mathcal{R})/d\mathcal{R} \geq 0$, then $\check{\mathcal{H}}(\mathcal{R})$ increases and $\overline{\mathcal{H}} - \check{\mathcal{H}}(\mathcal{R})$ and thus dm/dt are negative for large $\mathcal{R}$) or grow (if $d\check{\mathcal{H}}(\mathcal{R})/d\mathcal{R} \leq 0$) with the additional deformational work term. However the sign of $d\check{\mathcal{H}}/d\mathcal{R}$ and the amplitude of $\check{\mathcal{H}}$ cannot be chosen arbitrarily as they are constrained by the 2nd law of thermodynamics. Equation (111) leads to

$$\int_0^\infty \check{\mathcal{K}}(\mathcal{R}) \beta(\mathcal{R}) \left[\overline{\mathcal{H}} - \check{\mathcal{H}}(\mathcal{R}) \right] \mathcal{V}_{\mathcal{R}} d\mathcal{R} = f_c, \tag{119}$$

where $0 \leq f_c \leq 1$, which reduces to

$$\mathcal{B}^2 \left(\overline{\mathcal{H}} \, \overline{\mathcal{K}} - \overline{\mathcal{H}\mathcal{K}} \right) = f_c, \tag{120}$$

where, given (83),

$$\mathcal{B}^2 = \int_0^\infty \beta(\mathcal{R}) \mathcal{V}_{\mathcal{R}} d\mathcal{R} = \left(\int_0^\infty B(\mathcal{R}) \mathcal{V}_{\mathcal{R}} d\mathcal{R} \right)^2. \tag{121}$$

[115] The function

$$\check{\mathcal{H}} = f_c \frac{1}{\mathcal{B}^2} \frac{\check{\mathcal{F}}}{\overline{\mathcal{F}} \, \overline{\mathcal{K}} - \overline{\mathcal{F}\mathcal{K}}}, \tag{122}$$

obviously satisfies (120) for any function $\check{\mathcal{F}}$. The general expression for the grain evolution is therefore,

$$\dot{\mathcal{R}} = \frac{d\mathcal{R}}{dt} = \frac{\beta(\mathcal{R})}{4 \Pi \mathcal{R}^2 \rho} \left(\gamma \left[\overline{\mathcal{K}} - \check{\mathcal{K}}(\mathcal{R}) \right] + f_c \frac{\rho \Psi}{\gamma \mathcal{B}^2} \frac{\overline{\mathcal{F}} - \check{\mathcal{F}}(\mathcal{R})}{\overline{\mathcal{F}} \, \overline{\mathcal{K}} - \overline{\mathcal{F}\mathcal{K}}} \right). \tag{123}$$

[116] Employing the definitions for $\breve{\mathcal{K}}$, β and $\mathcal{B}^2$ given in (43), (83) and (121), and substituting the expression (85) for $B(\mathcal{R})$, we can express $\dot{\mathcal{R}}$ in terms of $\mathcal{R}$:

$$\dot{\mathcal{R}} = 2\gamma B_0^2 I_p \mathcal{R}^{p-2} \left[\overline{\mathcal{R}^{-1}} - \mathcal{R}^{-1} \right] + f_c \Psi \frac{\mathcal{R}^{p-2}}{8\Pi\gamma I_p} \left[\frac{\overline{\mathcal{F}} - \breve{\mathcal{F}}(\mathcal{R})}{\overline{\mathcal{F}} \, \overline{\mathcal{R}^{-1}} - \overline{\mathcal{F}\mathcal{R}^{-1}}} \right],$$
(124)

and recall that I_p is given in (87) and that barred (weighted average) quantities are given by (84). It is of course important to remember that all integrals and weighted averages of $\mathcal{R}^{-1}$ are time dependent as they depend on a grain size distribution that shifts and evolves during grain growth or grain reduction. Of course, when $\Psi = 0$, we return to the coarsening expression found in (86).

[117] Using the expression (124), we can readily show that the deformational work has an effect opposite to coarsening; while coarsening induces a mass flow from small grains to large grains, continuous damage does the opposite independently of the choice of $\breve{\mathcal{F}}(\mathcal{R})$. To prove this result, we must determine the sign of the quantity $\overline{\mathcal{F}} \, \overline{\mathcal{K}} - \overline{\mathcal{F}\mathcal{K}}$. The definition of the averaged quantities (see (84)) implies that

$$\mathcal{B}^2 \left(\overline{\mathcal{F}} \, \overline{\mathcal{K}} - \overline{\mathcal{F}\mathcal{K}} \right)$$
$$= \int_0^\infty \breve{\mathcal{F}} B \, dn \int_0^\infty \breve{\mathcal{K}}' B' dn' - \int_0^\infty B' dn' \int_0^\infty \breve{\mathcal{F}}\breve{\mathcal{K}} B \, dn$$
$$= \int\!\!\int_0^\infty BB' \breve{\mathcal{F}} \left[\breve{\mathcal{K}}' - \breve{\mathcal{K}} \right] dn dn'$$
$$= \frac{1}{2} \int\!\!\int_0^\infty BB' \left[\breve{\mathcal{F}} - \breve{\mathcal{F}}' \right] \left[\breve{\mathcal{K}}' - \breve{\mathcal{K}} \right] dn dn',$$
(125)

where the functions with primes are functions of $\mathcal{R}'$ (e.g., $B' = B(\mathcal{R}')$). The sign of $\breve{\mathcal{K}}(\mathcal{R}') - \breve{\mathcal{K}}(\mathcal{R})$ is $\text{sgn}(\mathcal{R} - \mathcal{R}')$, and $\breve{\mathcal{F}}(\mathcal{R}) - \breve{\mathcal{F}}(\mathcal{R}')$ has the sign of $\text{sgn}(\mathcal{R} - \mathcal{R}') \, d\breve{\mathcal{F}}/d\mathcal{R}$ (provided $\breve{\mathcal{F}}$ is monotonic). Therefore (125) implies that $\overline{\mathcal{F}} \, \overline{\mathcal{K}} - \overline{\mathcal{F}\mathcal{K}}$ has the sign of $d\breve{\mathcal{F}}/d\mathcal{R}$. For large grains $\overline{\mathcal{F}} - \breve{\mathcal{F}}(\mathcal{R})$ has a sign opposite to $d\breve{\mathcal{F}}/d\mathcal{R}$, so that $\left(\overline{\mathcal{F}} - \breve{\mathcal{F}}(\mathcal{R}) \right) / \left(\overline{\mathcal{F}} \, \overline{\mathcal{K}} - \overline{\mathcal{F}\mathcal{K}} \right)$ is always negative for large grains; similarly this factor is positive for small ones. This leads to the result that damage is thermodynamically required to involve reduction of large grains and growth of smaller ones, opposite to coarsening. Physically, this result shows that if damage creates more surface energy it must do so by increasing the population of smaller grains, which is accomplished by shrinking large grains and distributing their mass over small-grain populations.

7.1.2. General Behavior During Continuous Grain Damage

[118] We have already seen that coarsening implies the growth of large grains and the diminution of small ones. This process is associated with a reduction of grain population (by more of the mass existing in few larger grains and by the formation of vanishingly small grains); but since the decrease in grain number (the rate of which for the continuous coarsening case goes as $-d\dot{\mathcal{R}}/d\mathcal{R}$) is faster for small grains than for large grains, the mode of the distribution moves toward larger grain size (see Figure 4).

[119] The mechanism of continuous damage functions in the opposite sense. Since grains larger than the mean size shrink and those smaller than the mean grow, the grain size distribution naturally converges toward the mean (see Figure 4). The major effect of this continuous damage term is thus simply to narrow the width and increase the amplitude of the initial distribution. This homogenization of grain sizes accelerates with time since the denominator $\overline{\mathcal{F}} \, \overline{\mathcal{K}} - \overline{\mathcal{F}\mathcal{K}}$ tends to zero as the distribution becomes singular (i.e., becomes the distribution for homogeneous grain size).

[120] This mechanism of homogenization during deformation may not seem very realistic since it implies that a solid made of homogeneous grain sizes does not evolve when deformed. However, the homogenization of grain sizes during deformation is experimentally documented [*Faul and Jackson*, 2007]. In Figure 5, we show the evolution of a typical distribution under deformation, assuming arbitrarily that $\breve{\mathcal{F}}(\mathcal{R}) = \mathcal{R}^2$ and neglecting the coarsening term (or equivalently assuming $\Psi \gg 1$). To account for the fact that the coarsening term (which goes as $1/\mathcal{R}$) dominates at $\mathcal{R} = 0$, with $\dot{\mathcal{R}} < 0$, we impose a boundary condition of zero influx of grains at $\mathcal{R} = 0$. As expected, the grain size distribution becomes rapidly narrower, while the average grain size, remains mostly constant (it decreases by less than 0.1% in this numerical simulation).

7.2. Discontinuous Grain Damage

[121] The last simple case we examine corresponds to the case $\breve{f}_c = 0$, $\breve{f}_d \neq 0$; here we assume that there is no continuous exchange between grain populations ($\dot{\mathcal{R}} = 0$), but discontinuous exchange occurs through breaking and coalescence coupled with deformational work. The relevant system of equations is now

$$\int_0^\infty \left[-\frac{3}{2} \gamma \breve{\mathcal{K}} \breve{\mathrm{m}} \Gamma_\mathcal{M} + \breve{f}_d(\breve{\mathrm{m}}) \Psi \breve{\mathrm{m}} \mathcal{V}_\mathcal{M} \right] d\breve{\mathrm{m}}$$
$$= \gamma^2 \int\!\!\int_0^\infty G^d \left(\breve{\mathrm{m}}, \breve{\mathrm{m}}', \breve{\mathrm{m}}'', \breve{\mathrm{m}}''' \right)$$
$$\times \mathcal{A}\left(\breve{\mathrm{m}}, \breve{\mathrm{m}}' \right) \mathcal{A}\left(\breve{\mathrm{m}}'', \breve{\mathrm{m}}''' \right) dn dn' dn'' dn''' \geq 0,$$
(126a)

$$\int_0^\infty \breve{\mathrm{m}} \Gamma_\mathcal{M} d\breve{\mathrm{m}} = 0,$$
(126b)

$$\frac{d\mathcal{V}_\mathcal{M}}{dt} = \Gamma_\mathcal{M}.$$
(126c)

7.2.1. Rate of Grain Formation by Discontinuous Damage

[122] The general discussion on the source term, section 6.1 using the Smoluchowski aggregation formalism [*von Smoluchowski*, 1917] remains valid and thus (126a) leads to

$$\gamma \int\!\!\int_0^\infty E\left(\breve{\mathrm{m}}', \breve{\mathrm{m}}'' \right) \mathcal{A}\left(\breve{\mathrm{m}}', \breve{\mathrm{m}}'' \right) d\breve{\mathrm{m}}' d\breve{\mathrm{m}}'' + \int_0^\infty \breve{f}_d(\breve{\mathrm{m}}) \Psi \breve{\mathrm{m}} \mathcal{V}_\mathcal{M} d\breve{\mathrm{m}}$$
$$= \gamma^2 \int\!\!\int_0^\infty G^d \left(\breve{\mathrm{m}}, \breve{\mathrm{m}}', \breve{\mathrm{m}}'', \breve{\mathrm{m}}''' \right)$$
$$\times \mathcal{A}\left(\breve{\mathrm{m}}, \breve{\mathrm{m}}' \right) \mathcal{A}\left(\breve{\mathrm{m}}'', \breve{\mathrm{m}}''' \right) dn dn' dn'' dn''' \geq 0$$
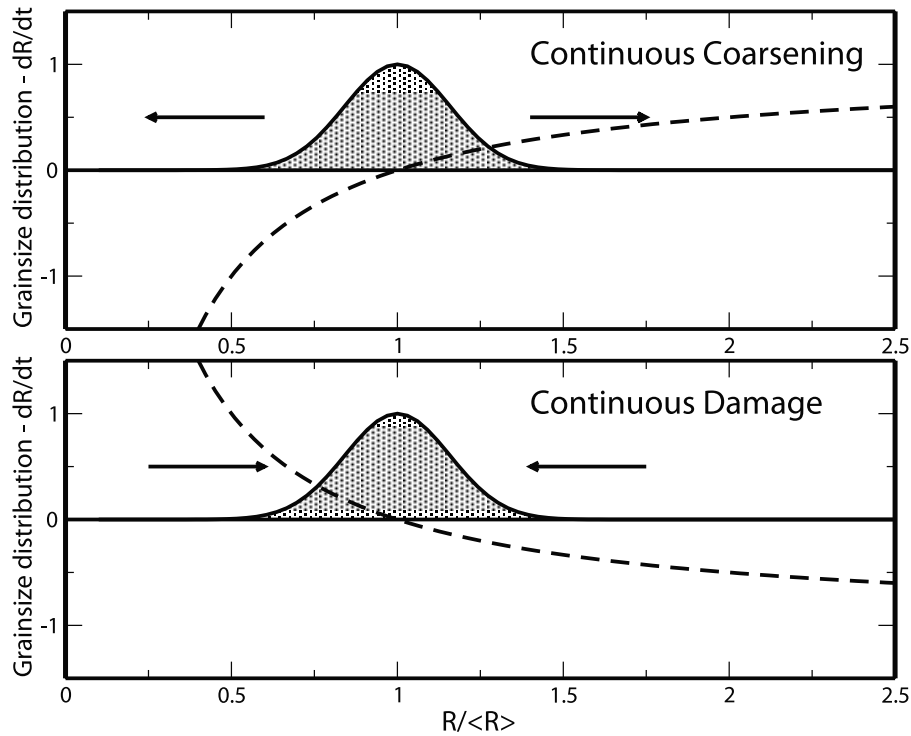(127)

Figure 4. Schematic evolution of a grain size distribution $\mathcal{V}_\mathcal{R}$ (shaded area) during continuous processes. The function $\dot{\mathcal{R}}$ is indicated by a dashed line. (top) Coarsening case: The function $\dot{\mathcal{R}}$ changes sign near $\mathcal{R} = \overline{\mathcal{R}}$ from negative to positive with increasing $\mathcal{R}$, and therefore, the grain size distribution diverges from $\overline{\mathcal{R}}$. However, the rate of change of grain population $d\mathcal{V}_\mathcal{R}/dt$ goes as $-\mathcal{V}_\mathcal{R}\partial\dot{\mathcal{R}}/\partial\mathcal{R}$ (see (16)), and thus, $\mathcal{V}_\mathcal{R}$ collapses asymmetrically about the mean, i.e., more rapidly for small $\mathcal{R}$ than for large $\mathcal{R}$; this causes the mode to shift to larger $\mathcal{R}$ and thus leads to an increase of the average grain size. (bottom) Damage case: The function $\dot{\mathcal{R}}$ varies in the opposite way, and the grain size distribution converges toward $\overline{\mathcal{R}}$. Depending on the curvature of $\dot{\mathcal{R}}$ (i.e., on the choice of $\mathcal{F}(\mathcal{R})$), the mode of the grain size distribution may slightly drift. However, this change in the average grain size remains very small because the distribution becomes rapidly singular around its initial $\overline{\mathcal{R}}$; this was also verified by an extensive suite of numerical simulations.

while as in (96), mass conservation (126b) is already accounted for by the expression for E, (94).

[123] The expression (94) for the reaction rate E includes a grain sticking rate $\Lambda_+ \left(\breve{m}', \breve{m}''\right)\mathcal{V}_\mathcal{M}(\breve{m}')\mathcal{V}_\mathcal{M}(m'')$ associated with a positive entropy source and a grain breaking rate $\Lambda_- \left(\breve{m}', \breve{m}''\right)\mathcal{V}_\mathcal{M}(\breve{m}' + \breve{m}'')$ associated with an entropy

sink. The entropy sink corresponding to Λ_- was disallowed in section 6.2 but is now permitted since it can be partially offset by the entropy production from deformational work (i.e., some fraction of work is used for breakage, which increases surface energy). In particular, employing (94) in
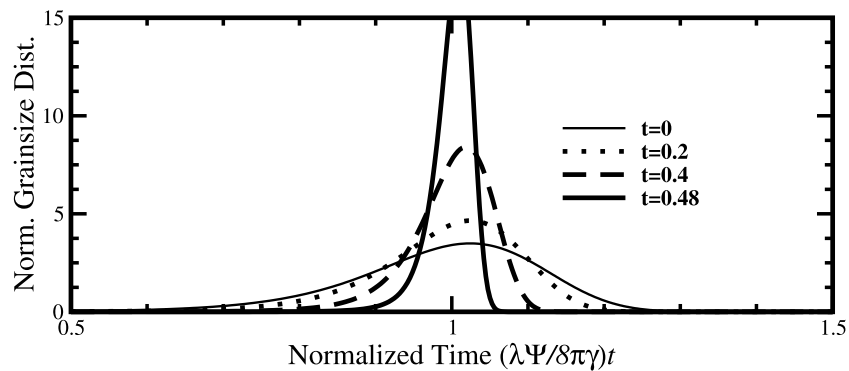

Figure 5. Evolution of the distribution of grain sizes $\mathcal{V}_\mathcal{R}(\mathcal{R})$ with time, assuming continuous damage. Instead of reaching a self-similar shape, the grain distribution converges toward a monodisperse peak. The average radius (not shown) varies by only negligible amounts and in a direction depending on the initial grain distribution.

(127), with the assumption that Λ_+ is still given by (100), then Λ_- must satisfy

$$\gamma \iint_0^\infty \Lambda_-(\check{m}',\check{m}'')\mathcal{A}(\check{m}',\check{m}'')\mathcal{V}_\mathcal{M}(\check{m}'+\check{m}'')d\check{m}'d\check{m}'' = f_d\rho\Psi, \tag{128}$$

with a macroscopic average partitioning factor f_d between 0 and 1.

[124] Just as we demonstrated in section 7.1.1 (see (120)–(123)), the function

$$\Lambda_-(\check{m},\check{m}') = \frac{f_d\rho\Psi}{\gamma}$$

$$\times \frac{\Lambda(\check{m},\check{m}')}{\iint_0^\infty \Lambda(\check{m}'',\check{m}''')\mathcal{A}(\check{m}'',\check{m}''')\mathcal{V}_\mathcal{M}(\check{m}''+\check{m}''')d\check{m}''d\check{m}'''}, \tag{129}$$

would satisfy the entropy requirements in (128) for any positive, symmetric function Λ. Therefore the general expression for the rate of grain formation by discontinuous damage alone is

$$\Gamma_\mathcal{M} = -\frac{f_d\rho\Psi}{2\gamma}$$

$$\times \frac{\iint_0^\infty \Lambda(\check{m}',\check{m}'')\Delta(m,m',m'')\mathcal{V}_\mathcal{M}(\check{m}'+\check{m}'')dm'dm''}{\iint_0^\infty \Lambda(\check{m}',\check{m}'')\mathcal{A}(\check{m}',\check{m}'')\mathcal{V}_\mathcal{M}(\check{m}'+\check{m}'')d\check{m}'d\check{m}''}. \tag{130}$$

7.2.2. An Example Solution for Grain Reduction With Damage

[125] To illustrate discontinuous grain reduction by damage, we simply assume that $\Lambda(\check{m}',\check{m}'')$ is a constant rate regardless of the mass of the generated subgrains $\check{m}'$ and $\check{m}''$ (note that in the numerator of general break, the integral has only to be performed until $\check{m}' + \check{m}'' = \check{m}$ since subgrains are obviously smaller than the initial broken grain). In this case,

$$\frac{d\mathcal{V}_\mathcal{M}}{dt} = \Gamma_\mathcal{M} = \frac{f_d\rho\Psi}{2\gamma} \frac{\int_0^\infty 2\mathcal{V}_\mathcal{M}(\check{m}+\check{m}')d\check{m}' - \check{m}\mathcal{V}_\mathcal{M}(\check{m})}{\iint_0^\infty \mathcal{V}_\mathcal{M}(\check{m}'+\check{m}'')\mathcal{A}(\check{m}',\check{m}'')d\check{m}'d\check{m}''}. \tag{131}$$

[126] Here again, self-similar solutions can be obtained, by inserting into (131) the expression $\mathcal{V}_\mathcal{M} = \rho/\overline{m}^2 H(\check{m}/\overline{m})$ (which itself arises from (10)). After some epiphanous algebra (using the same method as in Appendix B), we find that

$$H(u) = \exp(-u), \overline{m}^{-1/3} = \overline{m}_0^{-1/3} + \left(\frac{2}{9\pi\rho}\right)^{1/3}\frac{f_d\Psi t}{9\gamma\varpi}, \tag{132}$$

where now $u = \check{m}/\overline{m}$, and $\varpi = \iint_0^\infty (x^{2/3} + y^{2/3} - (x+y)^{2/3}) \exp(-x-y)\,dxdy \sim 0.065$.

[127] Figure 6 depicts the evolution of a characteristic distribution of grain size $\mathcal{V}_\mathcal{R} = 4\pi\mathcal{R}^2\rho\mathcal{V}_\mathcal{M}$ with time. The average grain mass (Figure 6, bottom) follows, as in the previous cases, the prediction of the analytical solution (132) (although the numerical solution is still far from the asymptotic $1/t^3$ behavior since the $\overline{m}_0$ term of (132) is not yet negligible). The normalized grain size distributions are shown in Figure 6 (top) as a function of the normalized radius $(\check{m}/\overline{m})^{1/3}$. The distributions are displayed at the normalized times 0, 0.2 and 0.4 and are evolving toward the self-similar solution, which (given that $\mathcal{V}_\mathcal{R} = 4\pi\mathcal{R}^2\rho\mathcal{V}_\mathcal{M}$) is

$$\mathcal{V}_\mathcal{R} \propto r^2 \exp(-r^3), \tag{133}$$

where $r = \mathcal{R}/\langle\mathcal{R}\rangle$ and $\langle\mathcal{R}\rangle = \overline{m}^{1/3}$. The same asymptotic distribution can therefore obtained by breaking grains (133) or sticking grains randomly (105), but of course the average grain size decreases in the first case and increases in the second case.

7.3. General Case

[128] There are four mechanisms that we have studied separately: two of them (continuous coarsening and discontinuous coalescence) operate in the static case and increase the mean grain size; and two of them (continuous grain reduction and discontinuous grain division) occur in the presence of deformation and damage and either homogenize the grain size distribution or decrease the mean grain size. In general, these mechanisms act simultaneously to affect the grain size distribution. Although we cannot explore all the possible combinations of these mechanisms, we can at least show a simple (and likely most common) case, i.e., when the grain growth is dominated by continuous coarsening through diffusive mass exchange (e.g., a normal grain growth theory in keeping with *Lifshitz and Slyozov* [1961] and *Wagner* [1961]), but where grain reduction is driven by damage through the discontinuous "breaking" mechanism. In this case the equation of grain size evolution is

$$\frac{\partial \mathcal{V}_\mathcal{M}}{\partial t} + \frac{\partial(\dot{\check{m}}\mathcal{V}_\mathcal{M})}{\partial\check{m}} = \Gamma_\mathcal{M} \tag{134}$$

where the coarsening rate $\dot{\check{m}} = 4\Pi\mathcal{R}^2\dot{\mathcal{R}}$ is given by (86) and the damage rate $\Gamma_\mathcal{M}$ is given by (131). The mechanism of coalescing grains should not be very efficient for crystalline solids, since the mismatch of atomic lattices between grains and the presence of secondary phases may prevent it.

[129] Although there is no self-similar asymptotic solution for this mixed case (as shown below), an interesting result can be found by substituting a trial solution $\mathcal{V}_\mathcal{M} = \rho/\overline{m}^2 H(\check{m}/\overline{m})$ into (134) (as with all cases, a scale factor of $1/\overline{m}^2$ is required by mass conservation).

[130] Since the Dirac δ functions of Δ have dimensions of $1/\check{m}$, the discontinuous source term with damage (131) becomes

$$\Gamma_\mathcal{M} = \frac{f_d\rho\Psi}{2\gamma}\left(\frac{2}{9\Pi\rho}\right)^{1/3}\overline{m}^{-5/3}H_a(u), \tag{135}$$

and the continuous (grain growth without damage) term,

$$
\frac{\partial\left(\dot{\check{m}}\mathcal{V}_{\mathcal{M}}\right)}{\partial\check{m}} = 8\Pi\gamma B_0^2 \rho^{(10-2p)/3}\overline{m}^{(2p-13)/3}H_b(u), \quad (136)
$$

where $H_a(u)$ and $H_b(u)$ are dimensionless shape functions of $u = \check{m}/\overline{m}$ related to derivatives of $H(u)$. The general grain size evolution therefore becomes

$$
-\frac{\rho}{\overline{m}^3}\frac{d\overline{m}}{dt}H_c(u) + 8\Pi\gamma B_0^2 \rho^{(10-2p)/3}\overline{m}^{(2p-13)/3}H_b(u)
$$
$$
= \frac{f_d\rho\Psi}{2\gamma}\left(\frac{2}{9\Pi\rho}\right)^{1/3}\overline{m}^{-5/3}H_a(u), \quad (137)
$$

where $H_c(u)$ is another dimensionless function related to $H(u)$.

[131] Asymptotic solutions can only be obtained if the variables are separable which is only possible if $(2p - 13)/3 = -5/3$ or $p = 4$, which is impossible since $p \leq 3$ (see Appendix A). Therefore no asymptotic solution exists with constant Λ_- (i.e., one cannot find functions $H_a(u)$, $H_b(u)$ and $H_c(u)$ satisfying (137)). Of course if Ψ or B_0 are zero, the variables are again separable and we can rederive the time evolution of $\check{m}$ (or $\mathcal{R}$), discussed in section 5.2 and section 7.2.1.

[132] The lack of existence of self-similar solutions implies that, in the presence of damage, there is no time-dependent grain size distribution that can be represented uniquely by the average grain size. This conclusion contradicts all earlier studies that treat only the evolution of the mean grain size to model the simultaneous processes of coarsening and grain reduction via dynamic recrystallization [e.g., *Karato et al.*, 1980; *Kameyama et al.*, 1997; *Montési and Hirth*, 2003; *Hirth and Kohlstedt*, 2003; *Braun et al.*, 1999; *Bercovici and Karato*, 2003]; in particular, these studies assume that the self-similar distribution during static grain growth, which allows description of the entire distribution by one grain scale such as the mean grain size, is relevant in the presence of deformation and damage. Our simple demonstration above shows this is not a valid assumption.

[133] Equation (137) presents, however, the interesting possibility of stationary solutions (i.e., $d\overline{m}/dt = 0$), which correspond to a state where the reduction of the grain size by damage is exactly balanced by diffusive coarsening. These solutions have the normalized shape determined by $H_a(u)/H_b(u) = $ constant (which is equivalent to a differential equation for $H(u)$) and an average grain size that satisfies

$$
\overline{\mathcal{R}}^{(2p-8)} \propto \left(\frac{\overline{m}}{\rho}\right)^{(2p-8)/3} \propto \frac{f_d\Psi}{\gamma^2 B_0^2}. \quad (138)
$$

[134] This result indicates that when a steady state regime is reached for the grain size distribution, the average grain size is a function of the deformational work, i.e., could be called a paleowattmeter [*Austin and Evans*, 2007]. The control of the grain size by the deformational work and damage has also been used by *Bercovici and Ricard* [2005] and *Landuyt et al.* [2008]. In the typical case $p = 2$, the stationary solution verifies $\overline{m} \propto \Psi^{-3/4}$ or $\overline{\mathcal{R}} \propto \Psi^{-1/4}$.

However since $\Psi = \tau^2/\eta$ where τ is a characteristic stress, and $\eta \propto \tau^{1-n}$ in the dislocation regime (with $n \approx 3$ [see, e.g., *Karato et al.*, 1980]), the paleowattmeter equation (138) becomes, in the dislocation regime, the piezometer

$$
\overline{\mathcal{R}} \propto \frac{1}{\tau^s}, \quad \text{where} \quad s = \frac{(n+1)}{(8-2p)}. \quad (139)
$$

For typical values of p and n (e.g., 2 and 3, respectively), the exponent s is of order 1 or slightly larger, which is in good agreement with observations [*Van der Wal et al.*, 1993].

[135] The evolution of the average grain size is depicted in Figure 7 (bottom) for various levels of viscous dissipation. In each case, except when $\Psi = 0$, the average grain size reaches an asymptotic limit proportional to $\Psi^{-1/4}$. In the case of $\Psi = 0$ (solid line), coarsening progresses indefinitively as $t^{1/3}$ (see section 5.1).

[136] The normalized steady state grain size distribution (Figure 7, top) is the same for all simulations (dotted lines). We depict both normalized distributions for grain size ($\propto \mathcal{V}_{\mathcal{R}}$, thin lines) and grain mass ($\propto \mathcal{V}_{\mathcal{R}}/\mathcal{R}^2$, thick lines) to emphasize the different behavior at small grain size. The steady solution (which is identical for all simulations of the Figure 7, bottom, that have reached their asymptotes for cases with $\Psi > 0$) is compared with the asymptotic self-similar solution obtained for the case of pure coarsening (90) and pure damage (133). Although the normalized shapes of the grain size distributions (thin lines) look similar, they differ significantly for small grain sizes, as readily shown by the grain mass distributions $\mathcal{V}_{\mathcal{M}} = \mathcal{V}_{\mathcal{R}}/\mathcal{R}^2$ (thick lines). In the cases with coarsening, the grain mass distributions go to infinity near $\check{m} = 0$ since the self-similar grain size distribution is $\propto \mathcal{R}$ near zero, hence $\mathcal{V}_{\mathcal{M}} \propto 1/\mathcal{R}$ (see (90)); for the case of pure damage, however, the self-similar grain size distribution is $\propto \mathcal{R}^2$ near zero, hence $\mathcal{V}_{\mathcal{M}}$ becomes constant (see (133)). Note that the three unnormalized distributions are very different since one distribution is steady and the two others correspond to self-similar solutions with a time-dependent average grain size (Figure 7).

8. Summary of Governing Equations

8.1. Macroscopic: Continuum Mechanical Equations

[137] Apart from the occasional appearance of surface tension related terms, the macroscopic equations differ little from the standard continuum mechanical equations. Since we have assumed that the medium is incompressible, the mass and momentum equations are given by (31) and (46), which we repeat here:

$$
\nabla \cdot \mathbf{v} = 0 \quad (140)
$$

$$
0 = \rho\mathbf{g} + \nabla \cdot \underline{\sigma} + \nabla(\gamma\mathcal{K}) \quad (141)
$$

where $\underline{\sigma}$ and $\mathcal{K}$ are the volume (or mass) averaged stress and grain boundary curvature ($\check{\mathcal{K}} = 2/\mathcal{R}$), as defined in (34) and (44), respectively. Stress $\underline{\sigma}$ itself is decomposed according to $\underline{\sigma} = -P\underline{I} + \underline{\tau}$, where P is the volume average of the grain pressure $\check{P}$, and $\underline{\tau}$ is the deviatoric stress. In addition to depending on gradients of the velocity field $\mathbf{v}$, $\underline{\tau}$
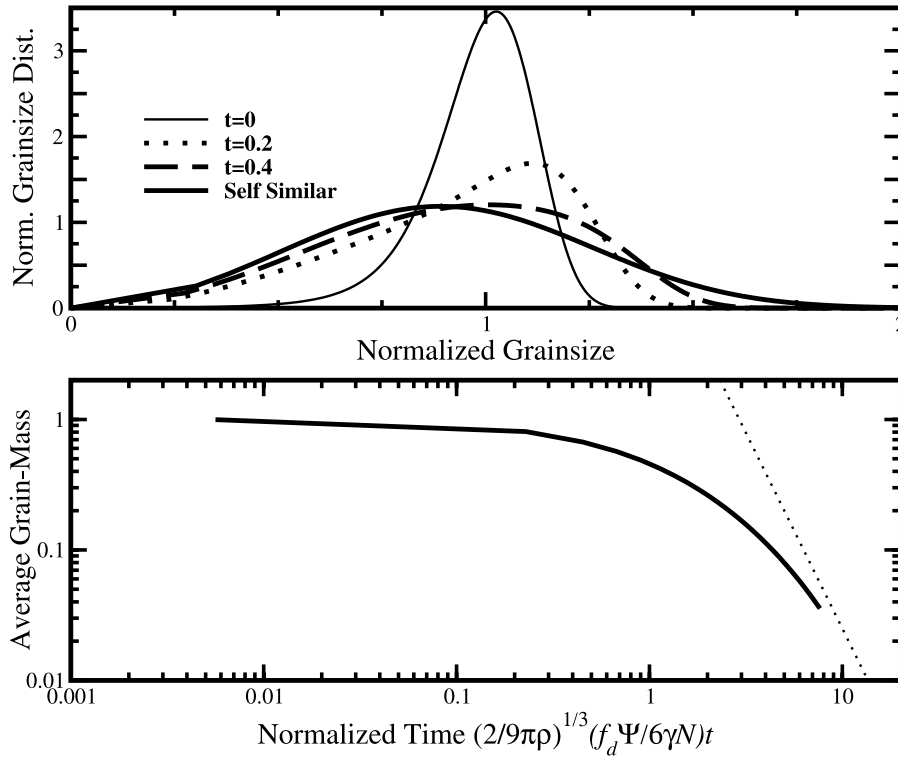
Figure 6. Evolution of the distribution of grain sizes $\mathcal{V}_{\mathcal{R}}(\mathcal{R})$ with time, in the grain breaking with damage case. (top) Normalized distribution as a function of the normalized grain size $\mathcal{R}/\overline{\mathcal{R}}$. The initial distribution evolves with time toward the self-similar distribution (thick solid curve). The other curves (dotted and dashed) correspond to intermediate times. (bottom) The average grain mass $\overline{m}$ follows the analytical prediction, (132), $\overline{m}^{-1/3} \propto t$. A slope of $-1/3$ is shown by the dotted line.

depends on viscosity which is a statistical average of grain viscosities. The viscosity is potentially a function of the whole grain size distribution (not just a function of $\overline{\mathcal{R}}$ as in more classical theories of diffusion creep or grain boundary sliding [see *Hirth and Kohlstedt*, 2003]) and of stress (as in dislocation creep). Both mean curvature $\mathcal{K}$ and viscosity are determined by the microscopic/statistical equations for coarsening and damage (summarized below in section 8.2).

[138] Although we did not explicitly develop a temperature equation, we can readily arrive at one from (63) by noting that because the medium is incompressible, then $d\breve{\varepsilon} = T d\breve{s} = c_v dT$ where c_v is heat capacity which we assume, like temperature T, is independent of grain size $\mathcal{R}$. In this case, (63) using the mass conservation (28) and the relation between macroscopic and microscopic derivatives (23), reduces to

$$\rho c_v \frac{DT}{Dt} = \Psi - \gamma \frac{D\alpha}{Dt} - \boldsymbol{\nabla} \cdot \mathbf{q} + \mathcal{Q} \qquad (142)$$

where α is the grain boundary area per unit volume. The expression for total entropy production is thus in agreement with (72) [see also *Bercovici et al.*, 2001a]. The temperature equation (142) is very similar to the standard temperature transport law (given that $\mathbf{q} \sim -\boldsymbol{\nabla} T$) except for the presence of the grain boundary energy effect wherein a loss of net grain boundary density α during coarsening results in an increase in temperature, while damage and grain size reduction will act to decrease temperature. As with $\mathcal{K}$ and viscosity, α is determined by the microscopic/statistical

equations for coarsening and damage. The formalism derived in this paper guaranties that the dissipation $\Psi - \gamma D\alpha/Dt$ remains a positive quantity.

8.2. Grain Scale: Statistical and Grain Growth Equations

[139] The grain scale, statistical model essentially reduces to three equations, the first for the evolution of the grain size distribution $\mathcal{V}_{\mathcal{R}}$, the second for the continuous grain growth kinetics (i.e., for $\dot{\mathcal{R}}$, by continuous changes of grain size through mass diffusion) and the third for the discontinuous transfer of grain population by breaking or coalescence (i.e., through the transfer rate $\Gamma_{\mathcal{R}}$). The grain size distribution equation (16) is repeated here:

$$\frac{D\mathcal{V}_{\mathcal{R}}}{Dt} + \frac{\partial(\dot{\mathcal{R}}\mathcal{V}_{\mathcal{R}})}{\partial\mathcal{R}} = \Gamma_{\mathcal{R}} \qquad (143)$$

[140] The evolution of $\mathcal{V}_{\mathcal{R}}$ depends on $\dot{\mathcal{R}}$ and $\Gamma_{\mathcal{R}}$, which are determined by

$$\dot{\mathcal{R}} = 2\gamma B_0^2 I_p \mathcal{R}^{p-2}\left[\overline{\mathcal{R}^{-1}} - \mathcal{R}^{-1}\right] + f_c \Psi \frac{\mathcal{R}^{p-2}}{8\Pi\gamma I_p}\left[\frac{\overline{\mathcal{F}} - \breve{\mathcal{F}}(\mathcal{R})}{\overline{\mathcal{F}}\,\overline{\mathcal{R}^{-1}} - \overline{\mathcal{F}\mathcal{R}^{-1}}}\right],$$
$$(144)$$

and by

$$\Gamma_{\mathcal{R}} = 2\Pi\mathcal{R}^2\rho \iint_0^\infty E(\breve{m}', \breve{m}'') \times \big(\delta(\breve{m} - \breve{m}' - \breve{m}'')$$
$$- \delta(\breve{m} - \breve{m}') - \delta(\breve{m} - \breve{m}'')\big) d\breve{m}' d\breve{m}'', \qquad (145)$$
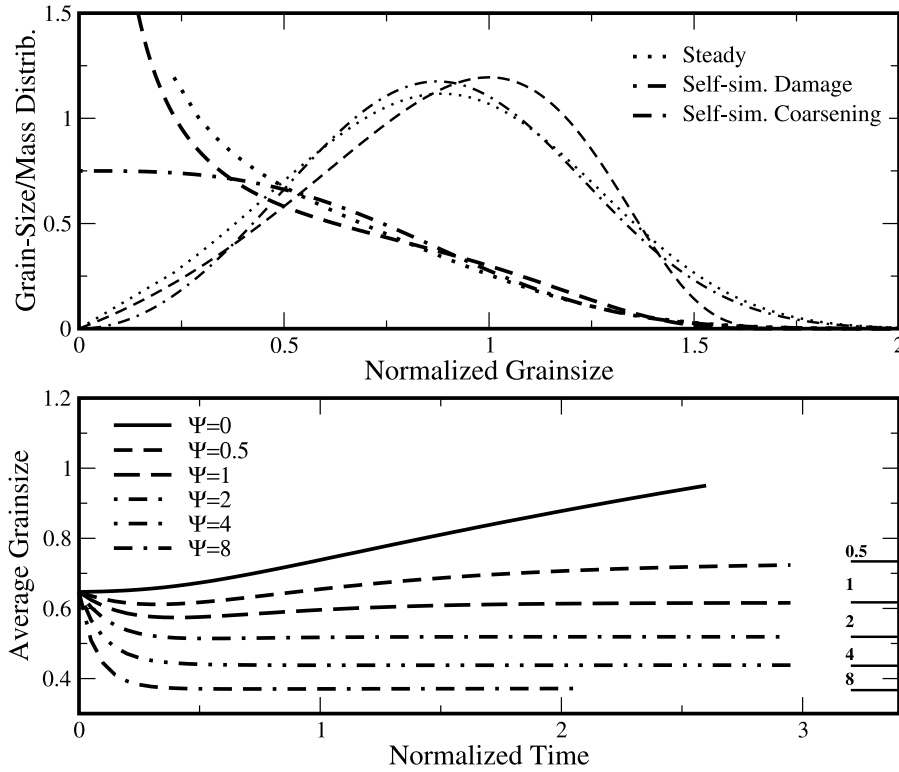
Figure 7. Evolution of the distribution of grain sizes with time in the simultaneous presence of coarsening and damage. (top) Normalized grain size (thin lines) and grain mass (thick lines) distributions as a function of the normalized grain size $\mathcal{R}/\overline{\mathcal{R}}$. The final steady state distribution (dotted line) is compared to the self-similar coarsening distribution (dash-dotted, also shown in Figure 2) and the self-similar damage distribution (dashed, also shown in Figure 5). The grain mass distributions (proportional to $\mathcal{R}^{-2}$ times the grain size distribution) illustrate the difference in behavior between $\mathcal{V}_{\mathcal{R}}$ and $\mathcal{V}_{\mathcal{M}}$ near $\mathcal{R} = 0$. (bottom) The evolution of the average radius is in agreement with (137). An asymptotic solution is reached, with the predicted value indicated by tick marks near the right vertical axis. Without damage (thick line, $\Psi = 0$), the expected $t^{1/3}$ behavior is recovered.

where the various parameters are defined in sections 7.1.1 and 6.1. In this last equation, the reaction rate is

$$E(\check{m}', \check{m}'') = \Lambda_+(\check{m}', \check{m}'')\mathcal{V}_{\mathcal{M}}(\check{m}')\mathcal{V}_{\mathcal{M}}(\check{m}'') \\ - \Lambda_-(\check{m}', \check{m}'')\mathcal{V}_{\mathcal{M}}(\check{m}' + \check{m}'') \quad (146)$$

where $\Lambda_+(\check{m}', \check{m}'')$ is the rate of grain sticking and is a symmetric and positive function (related to the loss of surface area, see (98) and (100)), and

$$\Lambda_-(\check{m}', \check{m}'') = \frac{f_d \rho \Psi}{\gamma} \\ \cdot \frac{\Lambda(\check{m}', \check{m}'')}{\displaystyle\iint_0^\infty \Lambda(\check{m}', \check{m}'')\mathcal{A}(\check{m}', \check{m}'')\mathcal{V}_{\mathcal{M}}(\check{m}' + \check{m}'')d\check{m}'d\check{m}''}, \quad (147)$$

is the rate of grain breaking (where Λ is another symmetric and positive function), and

$$\mathcal{A}(\check{m}', \check{m}'') = \left(\frac{9\Pi\rho}{2}\right)^{1/3}\left(\check{m}'^{2/3} + \check{m}''^{2/3} - (\check{m}' + \check{m}'')^{2/3}\right) \quad (148)$$

characterizes the change of surface area during grain creation or annihilation. The parameters f_c and f_d are positive and represent the fraction of energy removed from deformational work and stored as surface energy; the sum of these two quantities must be less than 1. Since $\dot{\mathcal{R}}$ and $\Gamma_{\mathcal{R}}$ are dependent on statistical averages of powers of $\mathcal{R}$, they are intrinsically dependent on the distribution $\mathcal{V}_{\mathcal{R}}$, and thus all the above equations are coupled. Moreover, with the inclusion of the deformational work or damage term proportional to Ψ in (144) and (147), the grain distribution and growth laws are coupled to the continuum mechanical laws outlined in section 8.1.

9. Discussion and Conclusions

[141] In this paper we have developed a new continuum theory of a grained medium with the purpose of describing, from first principles, shear localization and plate boundary generation associated with grain reduction.

[142] This theory is distinctly unlike dynamic recrystallization theories of shear localization which (1) treat only mean grain size and not grain size distribution; (2) treat grain growth (coarsening) under the influence of surface energy as if the system were static (even though it is moving and deforming and thus far from static); and (3) prescribe grain

reduction kinematically from empirical equations which do not necessarily satisfy basic mass and energy conservation.

[143] In contrast, the theory presented here derives entirely from basic continuum mechanical conservation laws and nonequilibrium thermodynamics; it describes the evolution of the full grain size distribution in a deformable and moving continuum; and it allows for nonstatic grain growth and change in grain number in the presence of both grain boundary surface energy as well as motion, deformation and damage. This is not to say that the theory presents a different mechanism from dynamic recrystallization but is instead a more general theory that potentially includes recrystallization amongst other possible mechanisms (e.g., cataclasis). The simulations that we have shown cover only a limited range of parameters and are presented to illustrate basic behavior. The various phenomenological coefficients are necessarily constrained by experiments designed to reveal the microscopic details of, for example, recrystallization and other microphysical effects.

[144] The theory presented here has considerable potential for understanding the complexities of localization in grained media like mantle/lithosphere rocks. One of the most important contributions of the theory is the inclusion of damage physics to the grain growth laws; this can predict not only how damage affects mean grain size but the entire grain size distribution, which is a testable prediction from deformation experiments. Indeed, the theory shows that the distribution of damage partitioning (the fraction of deformational work that goes into creating surface energy instead of dissipative heating) over grain sizes is thermodynamically required by the 2nd law of thermodynamics to have a specific trend; i.e., the damage partitioning must always drive large grains (above a critical grain size) to shrink and smaller ones to grow, and thus for the grain size distribution to either become narrower (as in section 7.1) or drift toward smaller grain sizes (as in section 7.2). The first mechanism of potential homogenization of grain size during deformation is surprising. The second mechanism of grain size reduction occurring under damage is perhaps more intuitively appealing, and it is reassuring that the intuitive solution is a thermodynamic requirement. Moreover, such a damage partitioning distribution gives credence to recent stipulations that simultaneous diffusion and dislocation creep in dynamic recrystallizing might occur in different parts of the grain size distribution, i.e., dislocation creep (and grain size reduction by recrystallization) in large grains and diffusion creep (and grain growth by coarsening) in smaller ones [*Bercovici and Karato*, 2003; S. Karato, personal communication, 2006].

Appendix A: Coarsening Self-Similar Solutions

[145] We assume for the grain size distribution a self-similar solution of the form $\mathcal{V}_\mathcal{R} = A(t)H(u)$, where $u = (\mathcal{R}/\langle\mathcal{R}\rangle)$ is a normalized grain size. This implies that when proper scalings are used for grain size (using $\mathcal{R}/\langle\mathcal{R}\rangle$) and grain distribution (using $\mathcal{V}_\mathcal{R}/A(t)$), the shape of the distribution ($H(u)$) is time independent. The conservation of mass, (10), implies a relation between A and $\langle\mathcal{R}\rangle$ such that

$$\mathcal{V}_\mathcal{R} = \frac{3}{4\Pi\langle\mathcal{R}\rangle^4}\frac{H(u)}{\lambda_3}. \tag{A1}$$

where it is convenient to introduce the various moments of the normalized grain size distribution,

$$\lambda_n = \int_0^\infty H(u)u^n du. \tag{A2}$$

[146] For the definition of $\langle\mathcal{R}\rangle$, we use

$$\langle\mathcal{R}\rangle = \int_0^\infty \mathcal{R}^p\mathcal{V}_\mathcal{R}d\mathcal{R} \Big/ \int_0^\infty \mathcal{R}^{p-1}\mathcal{V}_\mathcal{R}d\mathcal{R}, \tag{A3}$$

so that $\overline{\mathcal{K}} = 2/\langle\mathcal{R}\rangle$. Using (A1), the definition of $\langle\mathcal{R}\rangle$ implies that $\lambda_p = \lambda_{p-1}$. The individual grain size evolution equation for $\mathcal{R}$, (86) can therefore be rewritten

$$\dot{\mathcal{R}} = \frac{3B_0^2\gamma}{2\Pi}\frac{\lambda_p}{\lambda_3}\langle\mathcal{R}\rangle^{2p-6}u^{p-2}\left(1 - \frac{1}{u}\right). \tag{A4}$$

Using (A1) and (A4), the size evolution equation (73c) leads to

$$\langle\mathcal{R}\rangle^{6-2p}\frac{d\langle\mathcal{R}\rangle}{dt} = \frac{3B_0^2\gamma}{2\Pi}\frac{\lambda_p}{\lambda_3}u^3\frac{d}{du}\left(H(u)u^{p-2}\left(1 - \frac{1}{u}\right)\right)$$
$$\cdot\left[\frac{d}{du}\left(u^4H(u)\right)\right]^{-1}, \tag{A5}$$

where it is evident that the u- and t-dependent variables can be separated. We introduce the constant C, so that both sides of (A5) are equal to $(3B_0^2\gamma\lambda_p)/(2\Pi\lambda_3)\,C$. This shows that in the self-similar regime, the average radius varies like

$$\langle\mathcal{R}\rangle^{7-2p} = (7 - 2p)\frac{3B_0^2\gamma}{2\Pi}\frac{\lambda_p}{\lambda_3}Ct. \tag{A6}$$

The distribution shape $H(u)$ satisfies in turn

$$\frac{dH(u)}{H(u)} = \frac{(p-2)u^{p-3} - 4C - (p-3)u^{p-4}}{C + u^{p-4} - u^{p-3}}\frac{du}{u}. \tag{A7}$$

[147] The differential equation (A7) for $H(u)$ implies that near $u = 0$, the grain size distribution varies as $H(u) \sim 1/u^4$ if $p > 4$ and as $H(u) \sim u^{3-p}$ if $p < 4$. As we require that the mass of the distribution proportional to $\int_0^\infty u^3H(u)\,du$, converges, we must have $p < 4$. For $p < 4$, the grain size distribution cannot extend to $u \to \infty$ because (A7) predicts that $H(u) \sim u^{-4}$ if $p < 3$, or $H(u) \sim u^{2-p}$ if $3 < p < 4$. In both cases the mass in the distribution, which is proportional to $\int_0^\infty u^3H(u)du$, would not be convergent.

[148] The distribution $H(u)$ is therefore only defined for $p < 4$ and must have a finite domain $[0, u_0]$ where u_0 is the largest populated grain size. This maximum grain size is a constant in the similarity solution and its existence depends on the conditions for existence of a similarity solution [see *Lifshitz and Slyozov*, 1961; *Hillert*, 1965]. In particular, a similarity solution exists if the normalized growth rate is time independent, i.e., if $du/dt = 0$, or equivalently since $\langle\mathcal{R}\rangle$ is monotonic in t we can seek the conditions by which $\frac{\langle\mathcal{R}\rangle}{u}\frac{du}{d\langle\mathcal{R}\rangle} = 0$ (assuming this does not occur when either $\langle\mathcal{R}\rangle$ or u are 0). Since $u = \mathcal{R}/\langle\mathcal{R}\rangle$ then
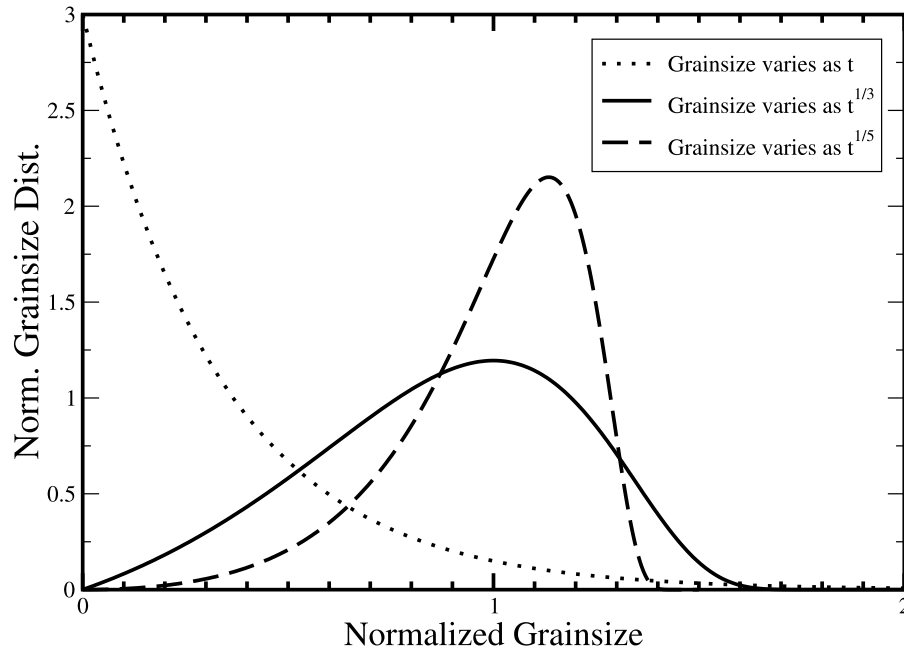
Figure A1. Examples of self-similar distributions for the case of continuous coarsening under static (nondeforming) conditions. The different curves represent three values of the parameter p (see (85)), which also controls the evolution of the average grain size with time (see inset legend); $p = 1$, 2, and 3 for the dashed, solid, and dotted curves, respectively.

$du/dt = \langle \mathcal{R} \rangle^{-1}(\dot{\mathcal{R}} - \langle \dot{\mathcal{R}} \rangle u)$, and using (A6) for $\dot{\mathcal{R}}$ and (A5) for $\langle \dot{\mathcal{R}} \rangle$ we find that

$$\frac{\langle \mathcal{R} \rangle}{u} \frac{du}{d\langle \mathcal{R} \rangle} = -\frac{3B_0^2 \gamma}{2\Pi} \frac{\lambda_p}{\lambda_3} \langle \mathcal{R} \rangle^{2p-6} \left[C + u^{p-4} - u^{p-3} \right] \quad (A8)$$

(the right side of which is the equivalent to the denominator in the factor of (A7) that multiplies du/u). The similarity solution exists for the narrow distributions infinitesimally close to u_0, which is a root of the right side of equation (A8). However, as argued by *Lifshitz and Slyozov* [1961] and *Hillert* [1965], the right side of (A8) must not only equal 0 but so must its derivative, i.e., u_0 must be a double root; the reason stated is that if this function crosses zero then normalized grain growth on either side of $u = u_0$ will be nonzero and either cause convergence of the population on this point, leading to singular distribution, or divergence from this point and thus zero population. A double root at $u = u_0$ allows a stable similarity solution for u near this point (since points infinitesimally close to u_0 have infinitesimal growth rates) that involve neither convergence nor divergence. Similarity solutions only exist for $u < u_0$ and for a constant C that satisfies $C + u_0^{p-4} - u_0^{p-3} = 0$ and $(p - 4) - (p - 3)u_0 = 0$. The second condition reduces further the domain of existence of similarity solutions to $p < 3$ (as $u_0 > 0$) and leads to the choice of

$$C = \frac{(3 - p)^{3-p}}{(4 - p)^{4-p}}, \quad \text{and} \quad u_0 = \frac{p - 4}{p - 3} \quad (A9)$$

(This double-root condition, discussed by *Lifshitz and Slyozov* [1961] and *Hillert* [1965], was critically reexamined by *Brown* [1989] and since, followed by a long-standing controversy [*Giron et al.*, 1998]; however, our numerical simulations (in the asymptotic limit of $t \to \infty$) are in agreement with this condition in.)

[149] After some cumbersome algebra, $H(u)$ can be found for several simple values of p (e.g., integers and half integers). Experimentally determined coarsening rates often imply $\langle \mathcal{R} \rangle \propto t^{1/3}$ [*Evans et al.*, 2001] thus p should be close to 2. For $p = 1$, 2 and 3, we get

$$H = \frac{u^2}{(3 + u)^{7/3}(3 - 2u)^{11/3}} e^{(3/(2u-3))}$$

$$\text{with} \quad \langle \mathcal{R} \rangle^5 = \frac{10 B_0^2 \gamma}{9\Pi} t, \quad \text{for} \quad p = 1$$

$$H = \frac{u}{(2 - u)^5} e^{(6/(u-2))}$$

$$\text{with} \quad \langle \mathcal{R} \rangle^3 = \frac{9 B_0^2 \gamma}{8\Pi} t \quad \text{for} \quad p = 2, \quad (A10)$$

$$H = \exp(-3u)$$

$$\text{with} \quad \langle \mathcal{R} \rangle = \frac{B_0^2 \gamma}{\Pi} t \quad \text{for} \quad p = 3,$$

(The solution for $H(u)$ with $p = 3$ is obtained in the limit where the double root $u_0 \to +\infty$).

[150] These functions are shown in Figure A1. As p decreases, the distributions become narrower around $u = 1$ (i.e., around $\mathcal{R} = \langle \mathcal{R} \rangle$). The mode moves to lower values of u as p increases and reaches $u = 0$ when $p = 3$. In principle,

experimentally determined static grain size distributions constrain the parameter p.

Appendix B: Discontinuous Grain Coalescence Self-Similar Solutions

[151] As in Appendix A, we look for solutions of the grain mass distribution evolution equation (102) of the form $\mathcal{V}_{\mathcal{M}}(\check{m}) = A(t)H(u)$ where now $u = \check{m}/\overline{m}$ and

$$\overline{m} = \frac{\int \mathcal{V}_{\mathcal{M}} \check{m}\, d\check{m}}{\int \mathcal{V}_{\mathcal{M}}\, d\check{m}}, \tag{B1}$$

(i.e., choosing $B(\check{m}) = 1$ in (84)). This definition of $\overline{m}$ implies that $H(u)$ satisfies

$$\int_0^\infty H(u)u\, du = \int_0^\infty H(u)\, du, \tag{B2}$$

while mass conservation (10) implies that

$$A(t) = A_0/\overline{m}^2, \quad \text{where} \quad A_0 = \rho \left(\int_0^\infty H(u)u\, du \right)^{-1}. \tag{B3}$$

[152] By substituting the self-similar representation for $\mathcal{V}_{\mathcal{M}}$ expression into

$$-\frac{A_0}{\overline{m}^3}\frac{d\overline{m}}{dt}\frac{1}{u}\frac{d}{du}\left(u^2 H(u)\right) = \frac{C_0 \gamma A_0^2}{\overline{m}^3}$$
$$\times \left(\frac{1}{2}\int_0^u H(u')H(u-u')du' - H(u)\int_0^\infty H(u')du' \right). \tag{B4}$$

As in Appendix A, the t- and u-dependent variables can be separated and the average mass must be simply proportional to t,

$$\overline{m} = \overline{m}_0 + Ct, \tag{B5}$$

where $\overline{m}_0 = \overline{m}$ $(t = 0)$ and C a constant. The asymptotic mass size distribution satisfies

$$-C\frac{1}{u}\frac{d}{du}\left(u^2 H(u)\right) = C_0 \gamma A_0$$
$$\times \left(\frac{1}{2}\int_0^u H(u')H(u-u')du' - H(u)\int_0^\infty H(u')du' \right). \tag{B6}$$

[153] This integrodifferential equation has solutions of simple exponential form since such functions can be factored from both sides of the equation; in particular, we obtain $H(u) = e^{-\alpha\, u}$ with $C = C_0\gamma\mathcal{A}_0/(2\alpha)$. Condition (B2) leads to $\alpha = 1$, while condition (B3) implies that $A_0 = \rho$. The asymptotic mass size distribution is therefore

$$\mathcal{V}_{\mathcal{M}}(\check{m}, t) = \frac{\rho}{\overline{m}^2}\exp\left(-\frac{\check{m}}{\overline{m}} \right), \tag{B7}$$

where the average mass size varies according to

$$\overline{m} = \overline{m}_0 + \frac{1}{2}C_0\gamma\rho t. \tag{B8}$$

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