# Prediction of Rate-Independent Constitutive Behavior of Pb-Free Solders Based on First Principles

P. Sharma, S. Ganti, A. Dasgupta, and J. Loman

***Abstract*—This paper presents a methodology for the theoretical estimation of rate-independent plastic constitutive properties of Pb-free solders using three approaches. The first approach is based on a nonlinear effective medium theory (NEMT) that is scale independent. The second approach is based on the micromechanics and physics of plastic slip in heterogeneous alloys (henceforth called the physical model). This approach explicitly includes microstructural features such as grain size, particle size etc. The third approach is a combination of NEMT and the physical model. Our estimates involve no adjustable calibration parameters and are based on first principles and constituent properties. Parametric studies are conducted to show that the physical model is more effective for small particles sizes (nanoscale $<100\ \mathrm{nm}$), small particle spacing ($\sim \mathrm{nm}$ range) and low volume fractions ($<2.5\%$); while NEMT performs well for large volume fractions ($>5\%$), large particle sizes (micron size) and large particle spacing (micron scale). The proposed hybrid approach, however, appears to be valid for a wider range of particle sizes and volume fractions. Limited comparison with experimental data is also made and implications of our work in the economical design of novel Pb-free solders is discussed.**

***Index Terms*—Heterogeneous alloys, hybrid, NEMT, Pb-free solders, physical model, plastic slip, viscoplastic materials, volume fractions.**

## I. Introduction

MEASURING the constitutive properties of complex nonlinear viscoplastic materials is a time consuming and expensive process. In the search for prospective Pb-free solder materials for electronic systems, there is a great need therefore for theoretical models that can predict such behavior based on first principles and microstructural features. This would greatly reduce the amount of testing needed, by allowing us to conduct many parametric studies through virtual testing. The potential application of such simulation capabilities would be to design, optimize, rank and down-select potential Pb-free solder alloys through model-based predictions of their expected behavior.

Researchers dealing with vibration or mechanical shock loading of electronic systems are interested in the nonlinear stress-strain response of solder materials at relatively high strain rates where dislocation slip mechanisms dominate rather than creep deformation mechanisms. This type of constitutive behavior is often termed "plastic" behavior and researchers often approximate this class of deformation behavior as "time-independent" or "rate-independent" or "instantaneous" behavior, as the characteristic time scales are extremely short. A power law, such as the Ramberg-Osgood law, is often used to describe the measured instantaneous stress-strain behavior. In this study we focus on this class of constitutive behavior.

In this paper, we use a hybrid combination of dislocation mechanisms (Orowan hardening, generation of geometrically necessary dislocations due to strain gradients and thermal residual stresses) and a secant nonlinear effective-medium homogenization method (Mori-Tanaka average matrix stress method), to demonstrate the effect of these alloying elements and alloying morphologies on the effective "instantaneous" stress-strain curves of different alloys. As an example, using the observed behavior of Sn3.5Ag Pb-free solder as an input, we demonstrate the ability to predict the behavior of Sn3.5Ag0.7Cu solder under the same loading conditions. The observed hardening in this instance is primarily due to dislocation hardening, but when the volume fraction of alloying elements increases, the effective medium effect, and interactions of these two effects can also play significant roles. Parametric studies are presented to demonstrate the effect of the volume fraction and particle size of the copper-rich phase.

Section II, we discuss the various physical mechanisms of rate-independent plasticity operative in metal composites and also provide a limited literature review. Section III, the three basic approaches to modeling the plasticity behavior of composites are formulated:

1) a nonlinear effective medium theory based on continuum mechanics;
2) a physical model based on dislocation mechanics;
3) a hybrid approach that is a combination of Approaches 1) and 2).

The validity of the model is tested on Sn3.5Ag0.7 Cu in Section IV and some parametric studies that illustrate the effect of particle size and volume fraction are presented. Finally, we conclude with a summary and discussion in Section V. In particular, some limitations of the current work are discussed and suggestions are made for future work.

## II. Mechanisms of Rate Independent Strengthening in Composites

Traditionally, metal matrix composites (and indeed Pb-free solders can be treated as composites), have been used to achieve higher strength in comparison to the matrix metal (i.e., Sn in our case). Even small amounts ($<1\%$ volume fraction) of stiff,

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strong particles have been known to cause appreciable increase in yield strength and hardening. Experiments clearly indicate that the overall inelastic behavior of the composites is strongly dependent on particle size and spacing and not just on the volume fractions [11], [16], [27]. In this section, we discuss the various possible physical mechanisms and their corresponding effects responsible for strengthening in composites.

1) Load Sharing: An obvious mechanism is the load sharing by the stiff particles. In the context of linear elasticity, in the last forty years, enormous amount of work has been done to account for elastic load sharing in the prediction of overall effective elastic properties of composites [12], [17]. The nonlinear plasticity problem is obviously more challenging as, unlike in the classic elasticity case, an analytical solution to the problem of an inhomogeneity in a nonlinear plastic matrix is not available (see [7] for the elastic case). Most classical elastic homogenization methods use Eshelby's fundamental solution as a starting point and apply various approximations to account for interactions between finite volume fractions of phases to predict the overall properties (e.g., self-consistent scheme, differential scheme, Mori-Tanaka mean-field approximation etc.). In the last decade and a half, some important results have begun to emerge regarding nonlinear effective properties. An entire monograph can be written on the existing literature on nonlinear behavior of composites and in the interest of brevity, we discuss only the most relevant papers.

   Some pioneering work can be traced to Hill [10] who extended the classical self-consistent scheme to plasticity in an incremental framework (which makes use of the elasto-plastic tangent modulus). The concept of secant modulus was introduced by Berveiller and Zaoui [4]. A major progress was made when Willis [26] and later Talbot and Willis [23] extended the linear Hashin-Shtrikman variational bounds to nonlinear materials. Subsequently Ponte Castaneda [19], [20] introduced a variational procedure that estimates effective nonlinear properties with the aid of a linear comparison material. The latter work provides the most rigorous bounds on nonlinear composites. In particular, these bounds coincide with the self-consistent scheme or the mean field Mori–Tanaka scheme, under certain circumstances [3], [14]. We finally conclude our brief literature review by noting that Suquet [21] proposed an alternative definition of effective phase strain or stress for the secant based method, namely the second moment of strain or stress, to account for the effects of volumetric deformation on rate-independent plasticity as well as improving the accuracy of predictions. Suquet's estimates, based on secant procedure involving the redefinition of effective strain coincide with the rigorous variational upper bound established by Ponte Castaneda [19]. For a more comprehensive review of this subject, the reader is referred to Suquet [22] and Ponte Castaneda [20].

   *Remark 1*: Continuum plasticity does not possess any intrinsic length scale and not surprisingly the results of ALL homogenization schemes are size independent. This will, of course become clearer in Section III where the formulation is described. Clearly, the scale-independency of the homogenization schemes is in contradiction with experiments that indicate that particle size and spacing play significant roles [11], [16], [27]. Thus, the homogenization schemes are appropriate when load sharing is the dominant mechanism.

2) Hardening due to Orowan Mechanisms: When a dislocation, while gliding along its slip plane, encounters an obstacle (say a particle), an additional stress is required to overcome the obstacle. Bowing of Orowan loops between two spaced particles is an example. At high temperatures of course, dislocation climb due to diffusion also becomes operative. The latter mechanism is not included in our work as we are mainly concerned with rate-independent plasticity. Using the concept of dislocation self-stress first discussed by Brown [5], Bacon *et al.* [2] have proposed a mechanistic model to estimate the additional stress required to bow out a dislocation loop from spaced particles. Material scientists have used this approximate model virtually unchanged since 1974 save for minor adjustments to account for particles distributions etc. A good overview of this model and related modifications can be found in [18]. The Orowan hardening process is schematically shown in Fig. 1.

3) Dislocation Hardening due to Thermal Residual Stresses: Due to mismatch between the particle coefficient of thermal expansion (CTE) and that of the matrix, residual plastic strains arise when the composite is cooled from its annealing temperature to room temperature. The residual plastic strains increase the dislocation density accounting partially for the increase in hardening of metal-matrix composites. The pioneering work in establishing relation between dislocation density increase and the thermal residual strains was done by Arsenault and Shi [1]. Their model, which is typically used by most researchers, is based on prismatic punching of dislocations at the parallelepiped particle-matrix interface.

4) Dislocation Hardening due to Geometrically Necessary Dislocations (GND): The presence of nearly rigid particles in a plastically deforming material gives arise to strong strain gradients. As explained very elegantly by Arsenlis and Parks (1999), the compatible deformation of the crystal gives rise to GNDs. In recent times, the increase in GND's due to plastic deformation and the consequent increase in yield strength has been a focus of several authors (e.g., Xue *et al.* [27], Duan *et al.* 2002, Nan and Clarke [16], Fleck *et al.* [8]). This concept was pioneered by Ashby (1970) and is now being used as the basis for the development of the so-called mechanism-based strain-gradient plasticity theory, that has an built-in size dependency unlike classical plasticity theory [9].

   *Remark 2:* Mechanisms 2–4 are scale dependent and their formulations (to be discussed in Section III) account explicitly for particle size, spacing and a few other microstructural features.

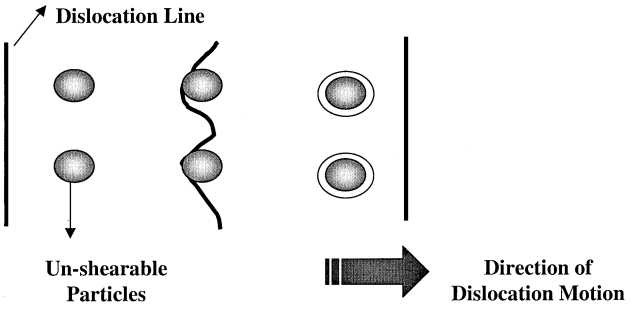


Fig. 1. Orowan hardening mechanism [18].

## III. Formulations

In this section we present the fundamental equations needed to implement the three modeling approaches discussed in Section I.

### *A. Approach 1: Homogenization Method Based on Continuum Micromechanics*

A comparison of various nonlinear homogenization schemes has been provided by Suquet [22]. We adopt here a secant formulation based on a modified definition of the effective strain [21]. We describe first the classical secant scheme and then introduce Suquet's modification.

In this scheme, the nonlinear constitutive law for the matrix is replaced by its secant modulus, i.e.,

$$\begin{aligned}\sigma &= \tilde{\mathbf{C}}_s(\varepsilon):\varepsilon \\ \tilde{\mathbf{C}}_s(\varepsilon) &= 3K\tilde{\mathbf{Q}} + 2\mu_s(\varepsilon_{eq})\tilde{\mathbf{R}} \\ \tilde{\mathbf{Q}} &= \frac{1}{3}\delta\otimes\delta; \\ R_{ijkh} &= \frac{1}{2}(\delta_{ik}\delta_{jh}+\delta_{ih}\delta_{jk}) - Q_{ijkh}. \end{aligned} \tag{1a-d}$$

The secant modulus, $\tilde{\mathbf{C}}_s$ is obviously a function of the strain. Upper case boldface Latin font with an overhead tilda indicates fourth-order tensors (the same tensors, in index notation, are in nonbold italic). Bold Greek symbols without overhead tildas are second order tensors. Both boldface and index notation are used as convenient. Conventional summation rules apply. $\sigma$ is the stress tensor while $\varepsilon$ is the strain tensor. The fourth-order tensors $\tilde{\mathbf{R}}$ and $\tilde{\mathbf{Q}}$ are projection tensors. $K$ is the isotropic bulk modulus and $\mu_s$ is the isotropic secant shear modulus. The bulk modulus is strain-independent under the assumption that for hydrostatic loadings, the response of the matrix is linear. The subscript "eq" refers to the definition of equivalent strain

$$\varepsilon_{eq} = \sqrt{\frac{2}{3}\mathbf{e}:\mathbf{e}}; \quad \mathbf{e} = \varepsilon - \frac{1}{3}tr(\varepsilon). \tag{2a-b}$$

The expression for the secant shear modulus is given in (3a)–(c) and our particular choice of constitutive law (multi-axial form of Ramberg-Osgood law) is indicated in (3d)

$$\begin{aligned}\mu_s(\varepsilon_{eq}) &= \frac{\sigma_{eq}}{3\varepsilon_{eq}}; \quad \sigma_{eq} = \sqrt{\frac{2}{3}\mathbf{s}:\mathbf{s}}; \\ \mathbf{s} &= \sigma - \frac{1}{3}tr(\sigma)\end{aligned}$$

$$\text{Ramberg-Osgood Law:}\varepsilon_{eq} = \frac{1}{3K}tr(\sigma) + \frac{\sigma_{eq}}{3\mu} + g\frac{\sigma_y}{E}\left(\frac{\sigma_{eq}}{\sigma_y}\right)^{1/n}. \tag{3a-d}$$

Here $g$ is a fitting parameter, $\sigma_y$ is the nominal yield stress of the matrix, $E$ is the Young's elastic modulus and $n$ is the hardening parameter. Consider now a two-phase composite containing a volume fraction $(f)$ of elastic reinforcements, subjected to a far-field uniform strain field, $\varepsilon^\infty$ (for an analogous formulation for traction boundary conditions [22]. The overall stress-strain behavior is given by

$$\bar{\sigma} = \bar{\tilde{\mathbf{C}}}_s(\varepsilon^\infty):\varepsilon^\infty. \tag{4}$$

An overhead bar indicates the overall properties or variables for the entire composite. The following results can be obtained for isotropic composites [22]:

$$\begin{aligned}\varepsilon^p(\varepsilon^m) &= \frac{1}{f}\left[\tilde{\mathbf{C}}^p - \tilde{\mathbf{C}}_s^m(\varepsilon^m)\right]^{-1}\left[\bar{\tilde{\mathbf{C}}}_s(\varepsilon^\infty) - \tilde{\mathbf{C}}_s^m(\varepsilon^m)\right]:\varepsilon^\infty \\ \varepsilon^m(\varepsilon^m) &= \frac{1}{1-f}\left[\tilde{\mathbf{C}}_s^m(\varepsilon^m) - \tilde{\mathbf{C}}^p\right]^{-1}\left[\bar{\tilde{\mathbf{C}}}_s(\varepsilon^\infty) - \tilde{\mathbf{C}}^p\right]:\varepsilon^\infty.\end{aligned} \tag{5a-b}$$

Here, the superscripts "$p$" and "$m$" indicate particle and matrix, respectively. Note that (5a-b) are nonlinear-coupled equations that are to be solved iteratively at each loading level. The fact that particles remain purely elastic in our study, simplifies the problem to some extent. If the particles also undergo plastic deformation, the particle moduli should also be replaced with their secant equivalents.

Our goal is to find the homogenized secant modulus of the composite. Virtually, any homogenization scheme for linear elastic materials can be used to obtain this at each loading level. We adopt the Mori–Tanaka mean-field concept [3], [14] and in such a case, the expression for effective moduli in terms of constituent moduli and Eshelby's tensor $(\tilde{\mathbf{S}})$ can be expressed as

$$\begin{aligned}\bar{\tilde{\mathbf{C}}}_s(\varepsilon^\infty) &= \tilde{\mathbf{C}}_s^m(\varepsilon^m) + f\left[\tilde{\mathbf{C}}^p - \tilde{\mathbf{C}}_s^m(\varepsilon^m)\right] \\ &\quad :\left[\tilde{I} + (1-f)P(\varepsilon^m):\left\{\tilde{\mathbf{C}}^p - \tilde{\mathbf{C}}_s^m(\varepsilon^m)\right\}\right]^{-1} \\ P(\varepsilon^m) &= \tilde{\mathbf{S}}:\tilde{\mathbf{C}}_s^m(\varepsilon^m).\end{aligned} \tag{6a-b}$$

The details of the Eshelby's tensor can be obtained from Mura [15]. Here, $\tilde{\mathbf{I}}$, is the identity tensor. The overall iterative scheme for solving the nonlinear equations in (5) is presented as a flowchart in Fig. 2. Suquet [21] proposed a simple modification to the secant formulation which results in improved accuracy at higher volume fractions (in case of particulate composites), and is able to capture the hydrostatic stress effects for porous materials. In the secant formulation, the strain field in each phase is replaced by its average value. Suquet proposed that the second moment of the strain be used instead, i.e.,

$$\begin{aligned}\text{Old definition: } \varepsilon_{eq}^m &= \langle\varepsilon_{eq}^m(x)\rangle \\ \text{Suquet's definition: } \varepsilon_{eq}^{m\times 2} &= \sqrt{\langle(\varepsilon_{eq}^m(x))^2\rangle}.\end{aligned} \tag{7a-b}$$

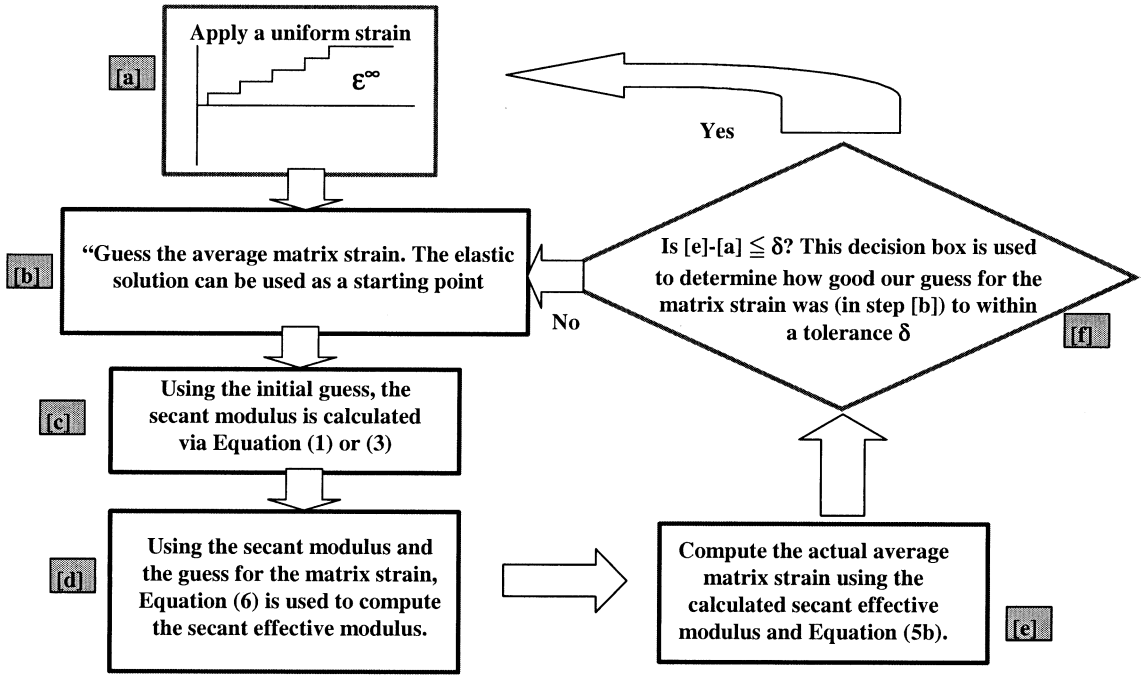


Fig. 2. Incremental-iterative procedure for nonlinear effective homogenization.

An expression for the second moment of phase strain for isotropic materials can be simply written as [22]

$$\varepsilon_{eq}^{m\times 2} = \sqrt{\frac{1}{1-f}\left[\frac{1}{3}\frac{\partial \bar{K}}{\partial \mu_s^m} tr(\varepsilon^{\infty})^2 + \frac{\partial \bar{\mu}_s}{\partial \mu_s^m}(\varepsilon_{eq}^{\infty})^2\right]}. \quad (8)$$

Equation (7b) is used instead of (2), in (3d) of this study, to provide higher accuracy.

### B. Approach 2: Physical Model

Surprisingly, within the context of dislocation-based physical modeling, most researchers use only first order (that are also closed-form) models to describe the effect of particles on increase in dislocation density. In general, researchers use Taylor's formula that relates the square root of the dislocation density to the additional stress required to cause dislocation movements

$$\Delta\sigma^{\text{hardening}} \propto \sqrt{\rho}. \quad (9)$$

Here $\rho$ is the dislocation density. The basis of the physical model is the estimation of dislocation density increase due to various mechanisms (except for Orowan mechanism).

*1) Orowan Hardening:* As mentioned earlier in Section III-A, the formula developed by Bacon *et al.* [2] is typically used for this mechanism. Although computer simulations, for example Mohles and Nembach [13], have resulted in some modifications, the original formulation provides a fair estimation for simple particle shapes and arrangement (as in our case). We can write the Orowan hardening stress as

$$\Delta\sigma^{Orowan} \cong \frac{\mu^m b}{2\pi\lambda(1-\nu)} \ln\left(\frac{b}{d}\right). \quad (10)$$

Here $d$ is the particle diameter, $b$ is the burgers vector and $\lambda$ is the average inter-particle spacing. This expression is only accurate to a first order and additional parameters (not thought to be important in our study) that can influence the hardening are: anisotropy of the matrix, mixed character of dislocations, particle distribution and so forth. The reader is referred to Nembach [18] for a recent review.

*2) Hardening Due to Thermal Residual Strains:* The pioneering model developed by Arsenault and Shi [1], is improved in this study. They consider the prismatic punching of dislocations from parallelepiped inclusions. They directly assume that the strain causing the dislocation punching is the product of the difference in the CTEs and the temperature excursion. Clearly the constraint of the matrix is not taken into account. Also, our particles (typically pure Cu phase or more realistically its intermetallics with Sn) are spherical shaped. Thus, we modify Arsenault and Shi's model in two ways:

1) matrix constraint is included;
2) the shape of the particles is assumed to be spherical rather than cuboidal.

We employ Eshelby's solution and treat the thermal mismatch as an eigenstrain. Further, making minor modifications to Arsenault and Shi's solution [1] to account for the spherical shape, we obtain

$$\text{Arsenault-Shi Model: } \rho^{\text{thermal}} = \left(\frac{12f}{bd}\right)(\Delta T \Delta\alpha)$$

$$\text{Our Model: } \rho^{\text{thermal}} = \left(\frac{6\pi f}{bd}\right) \times \left(\frac{fK^p}{3(1-f)(1+\nu)[(4\nu-2)K^m - (1+v)K^p]}\right) \times (\Delta T \Delta\alpha). \quad (11a\text{-}b)$$

The derivation of our model is described in Appendix I. The symbol $\alpha$ represents the CTE while $\nu$ is the Poisson's ratio.

The difference between our model and Arsenault-Shi's model is clear. The leading multiplier in each expression (11a–b) depends on the shape of the particle (cuboid versus sphere). The main difference is that the middle term, which is the elastic accommodation to the thermal mismatch, is absent in the Arsenault–Shi model. The incremental stress increase due to thermal mismatch hardening can be written as

$$\Delta\sigma^{\text{thermal}} = \mu^m b\sqrt{\rho^{\text{thermal}}}. \tag{12}$$

*3) Hardening Due to GNDs:* As discussed in Section III-B-II, geometrically necessary dislocations (GNDs) arise in the presence of strain gradients to maintain compatibility of deformation. In a single slip direction, the dislocation density due to matrix strain gradients can be written as

$$\rho^{GND} = \frac{1}{b}\frac{\partial\varepsilon^m}{\partial x}. \tag{13}$$

In the general sense, this equation is difficult to evaluate analytically as the matrix plastic strain (and hence the dislocation density) are nonuniform. Much work is in progress to derive reliable (and yet simple) estimates of the density of GNDs. For a review, see Arsenlis and Parks (1999). Combining with Taylor's formula, a first order version of (13) can be written as [6]

$$\Delta\sigma^{GND} = 0.4\mu^m\sqrt{\frac{f\varepsilon^m b}{d}}. \tag{14}$$

*Remark 3:* An important issue is the choice of how the various dislocation-based contributions should be combined. This is an important yet controversial question. The simplest solution would be to linearly add the additional stress from each physical mechanism to the virgin matrix yield stress. In this study, we follow the more intuitive approach of linearly adding the dislocation densities. Thus the incremental contributions to the yield stress are combined in a root-mean square fashion, except for the Orowan hardening (which does not vary with dislocation density within a first-order approximation). Mathematically

$$\Delta\sigma^{\text{total}} = \Delta\sigma^{Orowan} + \sqrt{(\Delta\sigma^{\text{thermal}})^2 + (\Delta\sigma^{GND})^2}. \tag{15}$$

*Remark 4:* Clearly, the physical model is scale-dependent, i.e., the particle size (and the related parameter, particle spacing) plays an important role. This feature was absent in Approach 1. On the other hand, load sharing is not taken into account in these models.

*Remark 5:* The limits of both Approaches 1 and 2 are clearly established by their inherent assumptions. Approach 1 is likely to be suitable when load sharing is dominant, i.e., for high volume fraction of particles and large particle size. Approach 2 is likely to be suitable when the volume fraction is small (in which case Approach 1 will hardly predict any improvement) or the particle size is small (Approach 1 is insensitive to particle size). Clearly, both approaches work only under certain limiting conditions.

### C. Approach 3: Hybrid Approach

An obvious extension of Approaches 1 and 2 would be a suitable combination i.e., a hybrid model valid at all particle sizes and volume fractions. Such a hybrid approach has been reported to be more successful than purely homogenization-based approaches or dislocation-based approaches in predicting experimentally observed results (Ramakrishnan, 1996; [16])[1] . Our approach differs in some respects from the approaches cited above. Ramakrishnan's (1996) approach can be considered to be more restrictive in the sense that

1) it only considers thermal residual strains as the hardening mechanism;
2) a fairly simplistic microstructure is used in the homogenization (spherical unit cell model);
3) the matrix is assumed to be elastic-perfectly plastic and thus work hardening is ignored.

Despite these simplifications, an iterative scheme is still required. On the other hand, our approach puts no restriction on the microstructure morphology (i.e., particles can be fibers, cylinders, ellipsoids and so forth). Shapes other than spherical can be trivially accounted for by substituting the appropriate Eshelby's tensor in (6). The details of Eshelby's tensor for various particle shapes (e.g., cylinders, ellipsoids , cuboids etc.) can be found in Mura [15]. Further, our matrix constitutive law allows power-law hardening and an attempt is made to consider all possible physical mechanisms and not just thermal residual strains.

The work of Nan and Clarke [16] is more similar to ours. However, their homogenization approach is based on the dilute assumption while we have followed the Mori–Tanaka mean field approach. Thus, interactions between particles cannot be adequately taken into account in their work (i.e., the formulation used by them becomes inaccurate at high volume fractions). Our hybrid approach is based on use of the mean-field based secant approach while using the modification of Suquet in conjunction with the physical models outlined in Approach 2. As noted before, this modified secant approach provides results that coincide with the rigorous variational upper bound of Ponte Castaneda [19]. Also our scheme for combining the various physical effects in (15) differs from that used by Nan and Clarke [16] who linearly add the stress increases due to the physical contributions.

In the context of Ramberg–Osgood constitutive law, the hybrid approach simply requires that the yield stress appearing in (3d) be replaced by the sum of the virgin matrix yield stress and the contributions from the physical mechanisms. Thus, as a result of dislocation hardening, the matrix material itself is considered to be altered and the homogenization proceeds on the dislocation-hardened matrix, i.e., the constitutive law in (3d) is replaced by

$$\varepsilon_{eq} = \frac{1}{3K}tr(\sigma) + \frac{\sigma_{eq}}{3\mu} + g\frac{(\sigma_y + \Delta\sigma^{\text{total}})}{E} \times \left(\frac{\sigma_{eq}}{\sigma_y + \Delta\sigma^{\text{total}}}\right)^{1/n}. \tag{16a-b}$$

## IV. Model Validation and Parametric Studies

The model is validated by comparing the predicted properties of Sn-3.5Ag-0.7Cu Pb-free solder with measured values. The Sn-3.5Ag Pb-free solder is used as the matrix and the effect of

[1]We have not considered additional papers by the same authors on account of the similarity of approach.

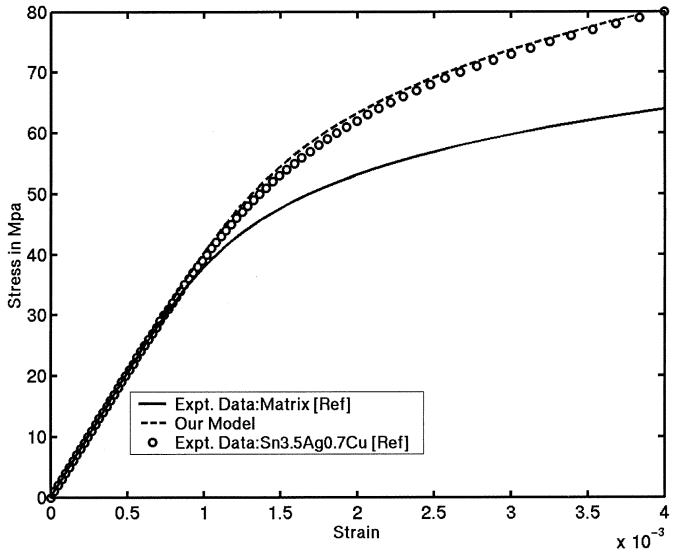


Fig. 3. Predictions for Sn3.5Ag0.7 Cu: Experimental results from [25].

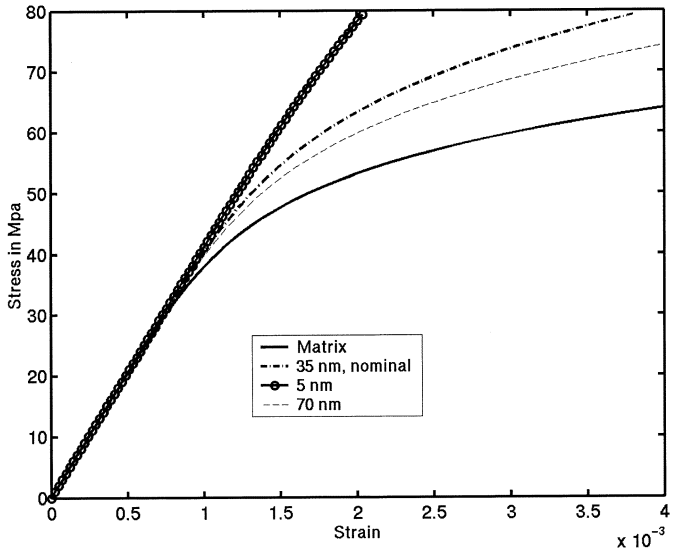


Fig. 4. Effect of particle size on effective stress-strain curve.

minute additions of copper (0.7%) are studied and compared with experiments. The results are shown in Fig. 3. Experimental data for the matrix and the final composite are obtained from Wiese *et al.* [25]. The particle size for Sn-Cu intermetallics is reported to range between 5 and 50 nm, with an average in the neighborhood of 30 nm[24]. We obtain an exact match with the experimental data for 35 nm particle size in our simulations.

The effects of particle size and volume fraction are demonstrated parametrically in Figs. 4 and 5, respectively. Fig. 4 shows the impact of particle size both on hardening and the yield stress, for a range of particle sizes 5–70 nm. The increase in hardening is also accompanied by a reduction in ductility. This is important since both contribute to fatigue endurance even in rate-independent failure mechanisms. Our model can provide an economical means for such an optimization. In Fig. 5, the effect of volume fraction is studied and the most striking observation is the significant impact on hardening even at relatively low volume fractions. Again, our model can be used to determine an optimum

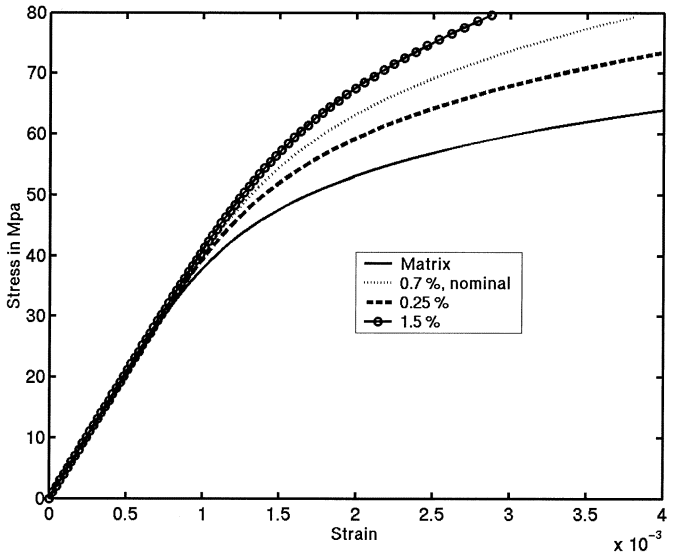


Fig. 5. Effect of particle volume fraction on effective stress-strain curve.

composition. This mechanistic optimization of course must be balanced against metallurgical considerations such as the eutectic composition for this ternary system.

## V. Conclsion

We have presented a hybrid approach that combines scale-independent homogenization for loading sharing with scale dependent dislocation mechanics to predict from first principles and constituent properties, the effective stress-strain curves for rate-independent plasticity in alloys such as solders. In particular, we have used the Mori–Tanaka method in a modified secant formulation compared to previous hybrid methods that either use the dilute scheme (which ignores interactions between particles at finite volume fraction) or the self-consistent scheme (which requires another iteration at each loading step). We have also extended the Arsenault–Shi model [1] for hardening due to residual plastic strains caused by thermal expansion mismatch. The new model takes into account the elastic accommodation of the matrix. Comparison with limited experimental data seems to validate the model.

At this point, it is also instructive to point out some of the limitations of the model and the possible ways to improve it. During this discussion, we may also allude to some of the features of the model that are deemed by the authors to be adequate.

1) The load sharing part of the model is thoroughly taken care of. The modified secant approach, together with the Mori–Tanaka scheme can provide results very close to finite element simulations and thus in the authors' opinion, further changes may be only of incremental value. If the volume fractions become extremely high, then other more implicit and advanced schemes may be employed, e.g., generalized self-consistent model (Nemat–Nasser and Hori, [17]). For typical volume fraction encountered in nanocomposites $(<20\%)$, this likely not an issue.
2) As was pointed out, the Orowan formula used in this paper is correct only to first order. Some of the modifications suggested in Mohles and Nembach [13] and

Nembach [18] may be incorporated to take into account particle distributions, matrix anisotropy, random arrangement of particles and so forth. Such models have been verified with detailed computer simulations by Mohles and Nembach [13].

3) We have modified Arsenault–Shi's original model to include matrix constraint. For small CTE mismatch, our formula is likely to be very close to the exact solution. In all other cases, it provides a rigorous lower bound to the hardening due to thermal residual plastic strains. No such claim can be made for the Arsenault–Shi model. Further improvement is possible by directly solving for nonuniform matrix plastic strains and subsequent averaging. Such an approach would be valuable if either the temperature excursion or the difference in CTE is very high.
4) By far the simplest model used in this paper is that for hardening caused by GNDs. A possible way to improve this model is suggested here. Solve exactly (analytically) for the plastic strains and strain gradients in the matrix, for a simple geometry (say spherical inhomogeneity). Formulate the nonuniform GND density and average over the matrix volume. Then, (optionally) some fitting parameters may be used to calibrate analytical results appropriately with finite element simulations. In this manner, other shapes can also be explored although analytical solutions are unlikely for general shapes. In such a situation, the spherical particle solution can be used as the analytical basis while shape factors are calculated numerically via finite element. Note that the procedure suggested above essentially averages over strain gradients in contrast to strain averaging in the first order model and an *ad hoc* selection of a length scale (i.e., particle size). The suggested procedure may yield a more accurate length scale parameter for GND density evolution.

In closure, we repeat that the current work is valid at high strain rates or low temperatures only (shock, vibration etc.). An analogous work is in progress for Pb-free solder applications where creep behavior is the dominant consideration. The implications for virtual testing and design of novel Pb-free solders are obvious.

## APPENDIX
## DERIVATION OF (11B)

Arsenault and Shi [1] show that for a cuboidal particle[2] the density of dislocations can be related to the residual plastic strain due to thermal mismatch as

$$\rho = \frac{2\varepsilon A_n}{b} A_s. \tag{17}$$

Here $A_n$ is the number of particles per unit matrix volume while $A_s$ is the surface area of the particle (cuboid in their Arsenault–Shi case). They define the plastic strain, $\varepsilon$, to be simply $\Delta T \Delta CTE$. This is clearly incorrect. This strain can only be achieved if the matrix provides no constraint. We reformulate this problem to consider the matrix constraint. We treat the thermal mismatch as an eigenstrain. Then according to Eshelby's formalism [7], the stress disturbance due to an elastic inhomogeneity embedded in an infinite elastic matrix (subjected to uniform far field strain $\varepsilon^0$—zero for the thermal residual problem) can be found by using the "equivalent inclusion" concept. Accordingly, an inhomogeneity can be replaced by an inclusion with a suitable fictitious eigenstrain prescribed within its domain. Let the inhomogeneity have a pre-existing inelastic strain (eigenstrain) $\varepsilon^p$ (in our case this will be the thermal eigenstrain). Then, this inhomogeneity can be replaced by an equivalent inclusion with a fictitious eigenstrain $\varepsilon^*$.

This fictitious eigenstrain is determined by solving the following equations within the region of the inhomogeneity $(V_\Omega)$

$$\begin{aligned}\mathbf{C}_{ijkl}(\varepsilon^o_{kl} + \mathbf{S}_{klmn}(\varepsilon^*_{mn} + \varepsilon^p_{mn}) - \varepsilon^*_{kl} - \varepsilon^p_{kl}) \\ = \mathbf{C}^h_{ijkl}(\varepsilon^o_{kl} + \mathbf{S}_{klmn}(\varepsilon^*_{mn} + \varepsilon^p_{mn}) - \varepsilon^p_{kl}).\end{aligned} \tag{18}$$

Here, $\mathbf{S}$ is the so-called Eshelby's tensor for interior points (i.e., all position vectors lying completely within the inhomogeneity). For an inhomogeneity of arbitrary shape, $\mathbf{S}$ is an integral operator on $(\varepsilon^* + \varepsilon^p)$ (Eshelby, [7]; Mura, [15]). In such a case, (18) are a set of six simultaneous integral equations that must be solved within the region of the inhomogeneity to determine the fictitious, (generally) nonuniform eigenstrain. In a classical elastic medium, Eshelby's tensor is uniform for certain shapes (e.g., ellipsoids which include spheres and cylinders). In such a case, (18) reduce to six algebraic equations, and the problem of an ellipsoidal inhomogeneity can be readily solved (Eshelby, [7]).

Since our thermal eigenstrain is purely of dilatational nature and there is no applied loading (the dislocation density increase due to thermal residual strain occurs during manufacturing, prior to any mechanical testing or application), we can separate out the deviatoric and bulk parts of (18) and directly evaluate the fictitious eigenstrain (after appropriately substituting Eshelby's tensor for spherical geometry)

$$\varepsilon^*_{kk} = \frac{-3K^p \varepsilon^p_{kk}(1-\nu)}{(4\nu-2)K^m - (1+\nu)K^P} - \varepsilon^p_{kk}. \tag{19}$$

The trace of the eigenstrain $\varepsilon^p$ in (19) is simply $3\Delta CTE\Delta T$. The actual strain can then be give by

$$\begin{aligned}\varepsilon_{ij}(\text{interior}) =& S_{ijkl}(\varepsilon^*_{kl} + \varepsilon^p_{kl}) \\ \varepsilon(\text{interior}) =& \left(\frac{1}{3}\right) tr(\varepsilon_{ij}) \\ =& \frac{K^p \Delta T \Delta CT}{3(1+\nu)[(4\nu-2)K^m - (1+\nu)K^p]}.\end{aligned} \tag{20a-b}$$

We, however, are interested in the matrix average strain. They satisfy the relation (in absence of far-field loading)

$$f\varepsilon_{ij}(\text{interior}) + (1-\text{f})\langle\varepsilon_{ij}(\text{matrix})\rangle = 0. \tag{21}$$

Equation (21) leads directly to (11b).

[2]Their analysis for a parallelepiped although without loss of generality we can consider their formula for a cube

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