

# Surface tension-driven shape-recovery of micro/nanometer-scale surface features in a $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ metallic glass in the supercooled liquid region: a numerical modeling capability

David L. Henann and Lallit Anand<sup>\*</sup> Department of Mechanical Engineering Massachusetts Institute of Technology Cambridge, MA 02139, USA

## Abstract

Recent experiments in the literature show that micro/nano-scale features imprinted in a Pt-based metallic glass, Pt<sub>57.5</sub>Ni<sub>5.3</sub>Cu<sub>14.7</sub>P<sub>22.5</sub>, using thermoplastic forming at a temperature above its glass transition temperature, may be erased by subsequent annealing at a slightly higher temperature in the supercooled liquid region (Kumar and Schroers, 2008). The mechanism of shape-recovery is believed to be surface tensiondriven viscous flow of the metallic glass. We have developed an elastic-viscoplastic constitutive theory for metallic glasses in the supercooled liquid temperature range at low strain rates, and we have used existing experimental data in the literature for Pt<sub>57.5</sub>Ni<sub>5.3</sub>Cu<sub>14.7</sub>P<sub>22.5</sub> (Harmon et al., 2007) to estimate the material parameters appearing in our constitutive equations. We have implemented our constitutive model for the bulk response of the glass in a finite element program, and we have also developed a numerical scheme for calculating surface curvatures and incorporating surface tension effects in finite element simulations. By carrying out full three-dimensional finite-element simulations of the shape-recovery experiments of Kumar and Schroers (2008), and using the independently-determined material parameters for the bulk glass, we estimate the surface tension of  $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$  at the temperature at which the shape-recovery experiments were conducted. Finally, with the material parameters for the underlying elastic-viscoplastic bulk response as well as a value for the surface tension of the Pt-based metallic glass fixed, we validate our simulation capability by comparing predictions from our numerical simulations of shape-recovery experiments of Berkovich nanoindents, against corresponding recent experimental results of Packard et al. (2009) who reported shape-recovery data of nanoindents on the same Pt-based metallic glass.

Key Words: Metallic glasses, Surface tension, Shape recovery, Viscoplasticity, Finite element method

## 1 Introduction

In a recent paper Kumar and Schroers (2008) have shown that in the metallic glass  $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ , which has a glass transition temperature  $\vartheta_g$  of 503 K (230°C), micron-scale features imprinted on the glass using thermoplastic forming at 523 K (250°C) could be erased by subsequent annealing in the supercooled liquid region at a temperature of 543 K (270°C). Figure 1 from their paper shows SEM images of two different micron-scale features, one with an as-printed height of  $\approx 5 \,\mu$ m, and another with an as-printed height of  $\approx 2 \,\mu$ m. This figure also shows images of the microfeatures after annealing at 543 K (270°C) for 60, 300, and 1200 s. A significant change in shape and height of the features is observed after only 60 s. Upon further annealing the features continue to decrease and merge into the base metallic glass, and after

<sup>\*</sup>Corresponding author. Tel.:+1-617-253-1635; E-mail address: anand@mit.edu

1200 s each feature is effectively *erased*, with the initially smaller feature erasing more completely than the larger feature. Kumar and Schroers (2008) propose that the kinetics of the decay in height of the pyramidal protrusions is determined by the initial height/curvature of the protrusions, the surface tension, and the viscosity of the metallic glass. They argue that the mechanism of shape-recovery is surface tension-driven viscous flow, with the surface tension driving the shape-recovery, which is opposed only by the low viscosity of the metallic glass in its supercooled liquid state.<sup>1</sup>

Kumar and Schroers (2008) suggest that the phenomenon of surface tension-driven shape-recovery has at least two possible applications: (i) in tandem with micro-hot-embossing, as a method of ultrahigh density rewritable data storage; and (ii) as a method of surface-smoothing of micron-scale metallic glass components. Each of these two prospective applications is discussed further below.

- (i) Currently, a method of ultrahigh-density data-storage is IBM's "millipede" system (Vettiger et al., 2002; Eleftheriou et al., 2003; Pozidis et al., 2004). In this data-storage technology, bits of information are written by indenting a thin *polymeric substrate* (typically PMMA) using an array of heated AFM cantilever tips. The AFM cantilever tips are heated to well above the glass transition of the polymer, and used to indent the polymeric substrate: a residual indent represents a "1", while an unindented region represents a "0". Instead of polymeric materials, metallic glasses may be used as an alternative substrate material, since these materials possess a much higher thermal conductivity than polymers, and they also possess the additional capability of surface tension-driven shape-recovery which may be used as a novel erasing mechanism thus allowing for the possibility of ultrahigh-density *re-writable* data-storage.
- (ii) Micro-patterned silicon tools, which are produced by deep-reactive-ion-etching (DRIE), are beginning to be used to thermoplastically form metallic glasses using a micro-hot-embossing process (Kumar et al., 2009; Henann et al., 2009). The corrugations left on the silicon master due to the DRIE process result in corrugated surfaces on the vertical side walls of metallic glass components produced by micro-hot-embossing. Surface tension-driven shape-recovery may be used to erase these unwanted features; cf. Figure 4 of Kumar and Schroers (2008). The surface tension-driven shape-recovery process may also be used to precisely control the dimensions of *intentionally produced* corrugated surfaces for use as optical gratings or microdies.

In order for these potential applications to be realized, a deeper scientific understanding of the phenomenon and a numerical simulation capability for surface tension-driven shape-recovery are necessary. The latter requires a constitutive theory for the bulk response of the material, as well as a method for calculating surface curvatures for arbitrary three-dimensional geometries, and a method for incorporating surface tension effects into the boundary conditions of the numerical solution methodology. Accordingly, the purpose of this paper is to (i) develop an elastic-viscoplastic constitutive theory for the metallic glass  $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$  in the super-cooled liquid temperature range relevant to the surface tension-driven shape-recovery process; (ii) develop a numerical method to calculate the curvature of *arbitrary surface geometries* and to account for the effects of surface tension as a suitable boundary condition; (iii) estimate the surface tension of  $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$  in the temperature range of interest; and (iv) demonstrate that our numerical simulation capability employing the constitutive model in conjunction with our method for incorporating surface tension effects is capable of reproducing the experimental results of shape-recovery of micro/nano-scale features recently reported in the literature.

This paper is organized as follows. In Section 2 we present a simple elastic-viscoplastic constitutive theory for metallic glasses in the super-cooled liquid temperature range at low strain rates, and in Section 3 we use the constitutive equations to derive an expression for the strain rate and temperature dependent non-Newtonian viscosity for metallic glasses in this strain rate and temperature regime. In Section 4 we use the experimental data of Harmon et al. (2007) for  $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$  to estimate the material parameters appearing in the constitutive equations for the bulk response of the metallic glass. We have implemented our constitutive model in the finite element program Abaqus/Standard (2008). In Section 5, we first describe our

 $<sup>^{1}</sup>$ One possible alternative explanation for the shape-recovery of microfeatures during annealing is atomic surface diffusion. However, this mechanism would be equally active in the crystalline and amorphous states, and as noted by Kumar and Schroers (2008), once the metallic glass crystallizes the process of shape-recovery halts. This leads them to state with confidence that the process is surface tension-driven.

numerical methodology for calculating surface mean curvatures and incorporating surface tension effects in finite element simulations. By carrying out three-dimensional finite-element simulations of the shape-recovery experiments of Kumar and Schroers (2008), and using the independently-determined material parameters for the bulk glass, we estimate the surface tension of  $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$  at the temperature at which the shape-recovery experiments were conducted. Finally, with the material parameters for the underlying elastic-viscoplastic bulk response as well as a value for the surface tension of the Pt-based metallic glass fixed, we validate our simulation capability by comparing predictions from our numerical simulations of shape-recovery experiments of Berkovich nanoindents, against corresponding recent experimental results of Packard et al. (2009) who reported shape-recovery data of nanoindents on the same Pt-based metallic glass.

## 2 Constitutive theory

Recently, Henann and Anand (2008) published a three-dimensional, elastic-viscoplastic, finite-deformation constitutive theory for metallic glasses in a high temperature range spanning the glass transition and for a large range of strain rates  $[10^{-5}, 10^{-1}] s^{-1}$ . In surface tension-driven shape-recovery processes, only temperatures above the glass transition, as well as relatively low strain rates ( $\sim 10^{-5}-10^{-3} s^{-1}$ ), are encountered. Accordingly, in this section we describe a simplified version of our theory for use in simulations of surface tension-driven shape-recovery processes are carried out under isothermal conditions, we limit our considerations here to isothermal situations in the absence of temperature gradients.

The underlying constitutive equations relate the following basic fields:<sup>2</sup>  $\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t)$ , motion;  $\mathbf{F} = \nabla \boldsymbol{\chi}, J = \det \mathbf{F} > 0$ , deformation gradient;  $\mathbf{F} = \mathbf{F}^e \mathbf{F}^p$ , elastic-plastic decomposition of  $\mathbf{F}$ ;  $\mathbf{F}^p, J^p = \det \mathbf{F}^p = 1$ , inelastic distortion;  $\mathbf{F}^e, J^e = \det \mathbf{F}^e > 0$ , elastic distortion;  $\mathbf{F}^e = \mathbf{R}^e \mathbf{U}^e = \mathbf{V}^e \mathbf{R}^e$ , polar decomposition of  $\mathbf{F}^e$ ;  $\mathbf{U}^e = \sum_{\alpha=1}^3 \lambda_{\alpha}^e \mathbf{r}_{\alpha}^e \otimes \mathbf{r}_{\alpha}^e$ , spectral decomposition of  $\mathbf{U}^e$ ;  $\mathbf{E}^e = \sum_{\alpha=1}^3 (\ln \lambda_{\alpha}^e) \mathbf{r}_{\alpha}^e \otimes \mathbf{r}_{\alpha}^e$ , logarithmic elastic strain;  $\mathbf{T}$ , Cauchy stress;  $\mathbf{M}^e = J^e \mathbf{R}^{e \top} \mathbf{T} \mathbf{R}^e$ , Mandel stress;  $\vartheta > 0$ , absolute temperature;  $\psi$ , free energy density per unit volume of the intermediate (or structural) space.

#### 1. Elasticity relations: free energy under isothermal conditions, equation for the stress

The free energy is taken in a simple quadratic form

$$\psi(\mathbf{E}^e, \vartheta) = G \left| \mathbf{E}_0^e \right|^2 + \frac{1}{2} K (\operatorname{tr} \mathbf{E}^e)^2, \qquad (2.1)$$

where the temperature dependent parameters

$$G(\vartheta) > 0 \text{ and } K(\vartheta) > 0$$
 (2.2)

denote the shear and bulk moduli, respectively. We assume that the Poisson's ratio  $\nu$  is independent of temperature; accordingly, the temperature dependent value of the bulk modulus may then be found by using the standard relation:

$$K(\vartheta) = G(\vartheta) \frac{2(1+\nu)}{3(1-2\nu)}.$$
(2.3)

Thus, the material parameters required to describe the elastic response are

$$\{G(\vartheta),\nu\}$$

The Cauchy stress is given by

$$\mathbf{T} \stackrel{\text{def}}{=} J^{e-1} \left( \mathbf{R}^{e} \mathbf{M}^{e} \mathbf{R}^{e^{\top}} \right), \tag{2.4}$$

<sup>&</sup>lt;sup>2</sup>Notation: We use standard notation of modern continuum mechanics. The symbols  $\nabla$  and Div denote the gradient and divergence with respect to the material point **X** in the *reference configuration*; grad and div denote these operators with respect to the point  $\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t)$  in the deformed configuration; a superposed dot denotes the material time-derivative. Throughout, we write  $\mathbf{F}^{e-1} = (\mathbf{F}^{e})^{-1}$ ,  $\mathbf{F}^{p-\top} = (\mathbf{F}^{p})^{-\top}$ , etc. We write sym**A**, skw**A**,  $\mathbf{A}_{0}$ , and sym<sub>0</sub>**A** respectively, for the symmetric, skew, deviatoric, and symmetric-deviatoric parts of a tensor **A**. Also, the inner product of tensors **A** and **B** is denoted by  $\mathbf{A} : \mathbf{B}$ , and the magnitude of **A** by  $|\mathbf{A}| = \sqrt{\mathbf{A} : \mathbf{A}}$ .

with

$$\mathbf{M}^{e} = \frac{\partial \psi(\mathbf{E}^{e}, \vartheta)}{\partial \mathbf{E}^{e}} = 2G\mathbf{E}_{0}^{e} + K(\operatorname{tr} \mathbf{E}^{e})\mathbf{1}.$$
(2.5)

The equivalent tensile stress for use in the viscoplasticity relations is defined by

$$\bar{\sigma} = \sqrt{3/2} \left| \mathbf{M}_0^e \right|. \tag{2.6}$$

### 2. Plasticity relations: flow rule

The evolution equation for  $\mathbf{F}^p$  is

$$\dot{\mathbf{F}}^p = \mathbf{D}^p \mathbf{F}^p, \qquad \mathbf{F}^p(\mathbf{X}, 0) = \mathbf{1},$$
(2.7)

with  $\mathbf{D}^p$  given by

$$\mathbf{D}^{p} = \sqrt{3/2} \,\dot{\bar{\epsilon}}^{p} \,\mathbf{N}^{p}, \qquad \mathbf{N}^{p} = \sqrt{3/2} \left(\frac{\mathbf{M}_{0}^{e}}{\bar{\sigma}}\right), \tag{2.8}$$

where

$$\dot{\tilde{\epsilon}}^p = \sqrt{2/3} \left| \mathbf{D}^p \right| \tag{2.9}$$

is an equivalent tensile plastic strain rate, given by a flow function

$$\dot{\bar{t}}^p = f(\bar{\sigma}, \vartheta) \ge 0. \tag{2.10}$$

Guided by the classical paper by Spaepen (1977) and following the recent paper by Henann and Anand (2008), the flow function for the equivalent tensile plastic strain rate is taken as<sup>3</sup>

$$\dot{\bar{\epsilon}}^p = \dot{\bar{\epsilon}}_0 \, \exp\left(-\frac{1}{\zeta}\right) \exp\left(-\frac{\Delta F}{k_B\vartheta}\right) \sinh\left(\frac{\bar{\sigma}V}{2k_B\vartheta}\right). \tag{2.11}$$

Here,  $\dot{\epsilon}_0$  is a pre-exponential factor of the order of the Debye frequency;  $\zeta$  is an "order-parameter" commonly called the "free volume";  $\Delta F$  is an activation energy;  $k_B$  is Boltzmann's constant; and V is an activation volume. The term  $\exp(-1/\zeta)$  in equation (2.11) represents a concentration of flow defects. At the low strain rates relevant to the surface tension-driven shape-recovery process, deformation-induced disordering is expected to be negligible. Accordingly, we assume here that the free volume  $\zeta$  is only a function of temperature, and take it to be given by the classical Vogel-Fulcher-Tammann (VFT) (Vogel, 1921; Fulcher, 1925; Tammann and Hesse, 1926) form

$$\zeta(\vartheta) = \frac{\vartheta - \vartheta_0}{B}, \qquad (2.12)$$

where B and  $\vartheta_0$  are constants. Thus the material parameters needed to describe viscoplastic flow of the glass are

$$\{\dot{\bar{\epsilon}}_0, B, \vartheta_0, \Delta F, V\}.$$

## 3 Non-Newtonian viscosity of metallic glasses

A notable feature of the experimentally-measured stress-strain response in simple compression experiments on metallic glasses conducted at a given temperature and strain rate is that after an initial transient *overshoot*, the stress level reaches a plateau and is essentially constant thereafter; this (near-)constant stress-level is called the *steady-state stress*. For such a fully-developed flow at a given temperature  $\vartheta$  and axial strain-rate  $\dot{\epsilon}(=|\dot{\epsilon}|)$ , when the stress reaches a steady-state "plateau" value  $\sigma_{ss}(=|\sigma|)$  and  $\dot{\epsilon} \approx \dot{\epsilon}^p$ , equation (2.11) for a one-dimensional situation may be inverted to read

$$\sigma_{ss} = \frac{2k_B\vartheta}{V}\sinh^{-1}\left(\frac{\dot{\epsilon}}{\dot{\epsilon}_0}\exp\left(\frac{B}{\vartheta-\vartheta_0}\right)\exp\left(\frac{\Delta F}{k_B\vartheta}\right)\right).$$
(3.1)

<sup>&</sup>lt;sup>3</sup>A flow function of this type was successfully used by Henann and Anand (2008) for the metallic glass  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  (Vitreloy-1) in a temperature range spanning the glass transition.

Equation (3.1) may then be used to define a strain rate and temperature-dependent *non-Newtonian shear* viscosity

$$\eta\left(\dot{\epsilon},\vartheta\right) \stackrel{\text{def}}{=} \frac{\sigma_{\text{ss}}}{3\dot{\epsilon}} = \frac{2k_B\vartheta}{3V\dot{\epsilon}} \sinh^{-1}\left(\frac{\dot{\epsilon}}{\dot{\epsilon}_0}\exp\left(\frac{B}{\vartheta-\vartheta_0}\right)\exp\left(\frac{\Delta F}{k_B\vartheta}\right)\right). \tag{3.2}$$

Note that under high temperatures and low strain rates, the inverse hyperbolic sine term in equation (3.2) may be approximated by its argument to obtain an expression for a Newtonian viscosity which is only a function of temperature,

$$\eta_{\text{Newtonian}}\left(\vartheta\right) = \frac{2k_B\vartheta}{3V\dot{\epsilon}_0} \exp\left(\frac{B}{\vartheta - \vartheta_0}\right) \exp\left(\frac{\Delta F}{k_B\vartheta}\right).$$
(3.3)

# 4 Material parameters for the metallic glass Pt<sub>57.5</sub>Ni<sub>5.3</sub>Cu<sub>14.7</sub>P<sub>22.5</sub>

We have estimated the material parameters appearing in our constitutive theory for  $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$ from the data published by Harmon et al. (2007) for this material. Although Harmon et al. (2007) provide data for the elastic shear modulus at various temperatures, they do so for temperatures in the range 470 to 503 K ( $\equiv \vartheta_g$ ) but not for temperatures above the glass transition temperature of this material. For our numerical simulations which are carried out at temperatures in the supercooled liquid region above  $\vartheta_g$ — based on previous experience with modeling metallic glasses (Henann and Anand, 2008) — we assume constant nominal values of

$$G \approx 10 \,\mathrm{GPa}, \quad \nu \approx 0.45,$$

$$(4.1)$$

for the elastic shear modulus and the Poisson's ratio, respectively. We emphasize that precise values of the elasticity parameters are *not crucial* for simulation of the shape-recovery process.<sup>4</sup>

In their Figure 1, Harmon et al. (2007) provide data for the strain-rate and temperature-dependent non-Newtonian viscosity  $\eta$  ( $\dot{\epsilon}$ ,  $\vartheta$ ), which they estimated from their compression experiments on Pt<sub>57.5</sub>Ni<sub>5.3</sub>Cu<sub>14.7</sub>P<sub>22.5</sub>. We have used their data to obtain the material parameters appearing in our constitutive equation (3.2); our curve-fitting procedure yields

$$\dot{\bar{\epsilon}}_0 = 9.0 \times 10^{11} \,\mathrm{s}^{-1}, \quad \Delta F = 5.47 \times 10^{-20} \,\mathrm{J}, \quad V = 1.28 \times 10^{-28} \,\mathrm{m}^3, \\ B = 2700 \,\mathrm{K}, \qquad \vartheta_0 = 400 \,\mathrm{K}.$$
(4.2)

The quality of the fit of equation (3.2) using the list of parameters (4.2) to the data of Harmon et al. (2007) is shown in Figure 2(a,b); the fit is quite reasonable. Figure 2(a) shows the viscosity as a function of strain rate for each of the temperatures for which data is reported in Harmon et al. (2007), and Figure 2(b) shows the viscosity as a function of temperature for several selected strain rates, where the number of strain rates for which data is plotted has been reduced for clarity. The Newtonian approximation (3.3) is also shown in Figure 2(b) as a dashed line. As is clear from this figure, the model nicely reproduces the important transition of the viscosity from a non-Newtonian response to a Newtonian response at the lowest strain rates as the material goes through the glass transition.

The constitutive theory described in Section 2 was implemented in Abaqus/Standard (2008) by writing a user-material subroutine (UMAT). This numerical implementation, together with the material parameters for the bulk response of  $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$  estimated here, is used in the next section to simulate the surface tension-driven shape-recovery experiments of Kumar and Schroers (2008). These simulations are used to *estimate* a value for the surface tension of this material in the supercooled liquid region.

## 5 Numerical simulations of surface tension-driven shape-recovery

In this section, we present our numerical simulations of surface tension-driven shape-recovery. First, we describe how surface tension boundary conditions are incorporated into our simulations. We then report on our estimate for the surface tension of  $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$  in the supercooled liquid region from the shape-recovery data of Kumar and Schroers (2008). Finally, with the material parameters for the underlying

 $<sup>^{4}</sup>$ Indeed numerical calculations show that the results from our shape-recovery simulations which use a value for the shear modulus of 10 GPa, are indistinguishable from those which are obtained by using a value of either 3 GPa or 30 GPa.

elastic-viscoplastic bulk response as well as a value for the surface tension of the Pt-based metallic glass fixed, we validate our simulation capability by comparing predictions from our numerical simulations of shape-recovery experiments of Berkovich nanoindents, against corresponding recent experimental results of Packard et al. (2009) who reported shape-recovery data of nanoindents on the same Pt-based metallic glass.

#### 5.1 Traction boundary condition for surface tension

Recall that with  $\mathbf{T}$  the Cauchy stress and  $\mathbf{n}$  the outward unit normal to the boundary of the body, the standard traction boundary condition is of the form

$$\mathbf{Tn} = \hat{\mathbf{t}} \quad \text{upon} \quad \mathcal{S}_t, \tag{5.1}$$

with  $\hat{\mathbf{t}}$  a given function of  $\mathbf{x}$  and t, and where  $S_t$  is the portion of the boundary  $\partial \mathcal{B}_t$  of the deformed body where the traction is prescribed. For example, if p is a prescribed scalar field, and if

$$\mathbf{Tn} = -p\,\mathbf{n} \qquad \text{upon} \qquad \mathcal{S}_t, \tag{5.2}$$

then the body is subjected to the *pressure* p upon  $S_t$ . An important special kind of pressure is that exerted by *surface tension*. The pressure due to surface tension reflects the nature of the body as well as its shape and nature of its surroundings, and is given by

$$p = 2 \gamma \kappa,$$

$$\kappa = \text{ mean curvature of } \mathcal{S}_t \text{ at } \mathbf{x},$$

$$\gamma = \text{coefficient of surface tension.}$$
(5.3)

Thus, equation (5.1) may be written as

$$\mathbf{Tn} = -2\gamma\,\kappa\,\mathbf{n} \qquad \text{upon} \qquad \mathcal{S}_t. \tag{5.4}$$

In our simulations we apply this normal traction to the load integration points on the free surface of the finite element model. This is done by programming an Abaqus subroutine called a DLOAD that allows for user-defined distributed loads, i.e. normal tractions. The primary tasks then reduce to (i) a calculation of the mean curvature  $\kappa$ , the details of which we relegate to an Appendix; and (ii) an estimation of the surface tension  $\gamma$ . We turn to this latter task in the next section.

## 5.2 Estimate of the surface tension of Pt<sub>57.5</sub>Cu<sub>14.7</sub>Ni<sub>5.3</sub>P<sub>22.5</sub>

Using the independently-determined material parameters for the bulk glass, we have estimated the surface tension of  $Pt_{57.5}Ni_{5.3}Cu_{14.7}P_{22.5}$  by carrying out full three-dimensional finite-element simulations of the shape-recovery experiments of Kumar and Schroers (2008), and adjusting the value of  $\gamma$  until the simulations are able to reproduce the shape-recovery experimental results reported by these authors.

In their experiments, Kumar and Schroers (2008) first indented a Zr-based metallic glass ( $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ ) substrate with a Vickers pyramidal indenter to three different depths, and then used the Zr-based glass with the indents as an embossing tool to generate pyramidal-shaped protrusions on the surface of a polished  $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$  substrate by hot-embossing at 523 K (250°C) at an applied pressure of 100 MPa.<sup>5</sup> To create the initial mesh for our shape-recovery simulations we follow a similar path; that is, we first simulate the embossing of the pyramid-shaped microfeatures into the  $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$  substrate, which is modeled using 32000 Abaqus-C3D8H elements.<sup>6</sup> Figure 3(a,b) shows the final shape after embossing.<sup>7</sup> Specifically, Figure 3(a) shows a three-dimensional perspective view of a pyramidal microfeature and the surrounding material, and Figure 3(b) shows a two dimensional projection of the side view of the domain. The initial height of the microfeature is denoted as  $h_0$ , and the surrounding material consists of a square

 $<sup>^{5}</sup>$ At this embossing temperature the Zr-based glass is well below its glass transition temperature of 623 K (350°C).

 $<sup>^{6}</sup>$ This was done primarily to generate a highly-structured initial mesh for our shape-recovery simulations. This affords a more accurate calculation of local curvature than if the surface mesh is unstructured.

 $<sup>^{7}</sup>$ A slight rounding of the edges of the pyramidal microfeature was introduced in order to ease the calculation of curvature in the vicinity of these edges.

 $b \times b$  domain of depth of t. Following the experiments of Kumar and Schroers (2008), we consider three different values of the initial height  $h_0$  of the pyramidal microfeatures:

4.67 
$$\mu$$
m, 2.86  $\mu$ m, and 1.55  $\mu$ m.

For the 4.67  $\mu$ m-high microfeature, we employ a base width of  $b = 60 \,\mu$ m and a base depth of  $t = 30 \,\mu$ m. The values of b and t are scaled appropriately for the smaller features.

For the shape-recovery simulations, symmetry boundary conditions were specified on the sides and bottom of the finite element mesh. Specifically, with respect to Figure 3, we set  $u_x = 0$  on sides ABCD and EFGH,  $u_y = 0$  on the sides BFGC and AEHD, and  $u_z = 0$  on the bottom CGHD. On the top surface, we applied the surface tension boundary condition described in the previous subsection. The pyramidal microfeatures of the three initial heights were "numerically annealed" at a temperature of 543 K (270°C) for 1200s, and the decay in the height of the pyramids versus annealing time was calculated. Several iterations of these simulations were run to match the corresponding data reported by Kumar and Schroers (2008) (their Figure 3), in order to determine a suitable value for the surface tension. The value that best fit their experimental data was

$$\gamma = 0.19 \, \text{N/m}.$$

Figure 4 shows the feature height h of each of the three microfeatures as a function of time. The symbols are experimental data from Kumar and Schroers (2008), and the dashed lines are the results from our numerical simulations using the independently-determined material parameters for the bulk glass, and the value of the surface tension  $\gamma$  listed above. The quantitative agreement between the simulations and the experimental data is quite good.

Figure 5(a) from Kumar and Schroers (2008), shows SEM images of the largest pyramidal microfeature  $(h_0 = 4.67 \,\mu\text{m})$  at various times; viz., the initial shape, and after annealing for 60, 300, and 1200 s. Figure 5(b) shows corresponding images of the microfeature from our numerical simulations at the same times. The numerically-calculated evolution of the shape of the microfeature compares favorably with that which is experimentally observed.

Thus, using a calibrated constitutive model for the elastic-viscoplastic response of the bulk material, and our numerical modeling capability for applying surface-tension related traction boundary conditions on free surfaces, one can use three-dimensional finite-element simulations of shape-recovery to *determine* the surface tension of Pt<sub>57.5</sub>Cu<sub>14.7</sub>Ni<sub>5.3</sub>P<sub>22.5</sub>. The value of surface tension  $\gamma$  so obtained, is expected to be as accurate as the independent experimental measurements of the non-Newtonian viscosity and the shape-recovery response.

#### 5.3 Validation of the simulation capability

Here we report on our study to validate our simulation capability. Specifically, we compare predictions from our numerical simulations of shape-recovery experiments of Berkovich nanoindents, against corresponding recent experimental results of Packard et al. (2009) who reported shape-recovery data of nanoindents on the same Pt-based metallic glass.

As in the previous section, the initial mesh was obtained by first simulating the indentation of a  $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$  substrate with a Berkovich tip. As before, the metallic glass substrate was modeled using 32000 Abaqus-C3D8H elements. Figure 6(a,b) shows the final shape after indentation which is used as the initial mesh for our shape-recovery simulations. Figure 6(a) shows a three-dimensional perspective view of the residual Berkovich indent and the surrounding material, and Figure 6(b) shows a two-dimensional projection of the side view of the domain. The initial depth of the residual indent is denoted as  $h_0$ , and the surrounding material consists of a square  $b \times b$  domain with a depth of t. Following the experiments of Packard et al. (2009), we consider different values of the initial depth  $h_0$  of the indent:

$$264 \,\mathrm{nm}, 180 \,\mathrm{nm}, \text{and} 146 \,\mathrm{nm}.$$

For the 264 nm-high microfeature, we employ a base width of  $b = 5 \,\mu\text{m}$  and a base depth of  $t = 2.5 \,\mu\text{m}$ . The values of b and t are scaled appropriately for the smaller features.

For the recovery simulations, symmetry boundary conditions were specified on the sides and bottom of the finite element mesh. Specifically, with respect to Figure 6, we prescribed  $u_x = 0$  on sides ABCD and EFGH,  $u_y = 0$  on the sides BFGC and AEHD, and  $u_z = 0$  on the bottom CGHD. On the top free surface, we applied the surface tension boundary condition described previously. The indented specimens of initial heights  $h_0 = 264 \text{ nm}$  and  $h_0 = 180 \text{ nm}$  were "numerically annealed" at a temperature of 523 K (250°C) for 3600 s, and the indented specimen of initial height  $h_0 = 146 \text{ nm}$  was "annealed" at 513 K (240°C) for 3600 s. Figure 7(a,b) shows the indent depth h as a function of annealing time for the indents annealed at 523 K and 513 K, respectively, along with the corresponding experimental measurement by Packard et al. (2009). The agreement between the simulations and the experimental data is quite reasonable.<sup>8</sup>

Figure 8(a) from Packard et al. (2009) shows topographic contour plots of the largest residual Berkovich indent ( $h_0=264$  nm) annealed at 523 K (250°C) at various times, viz., the initial shape, and after annealing for 20 minutes, 30 minutes, and 60 minutes. Figure 8(b) shows corresponding topographic contour plots of the residual indent from our simulation.<sup>9</sup> The numerically-calculated shape-recovery of the indent compares favorably with that which is experimentally observed.

Thus, using the value of surface tension determined in the previous section for the annealing of *micron-sized* four-sided pyramidal protrusions at 543 K (270°C), one can reasonably accurately predict the shape-recovery behavior of *nanometer-sized* three-sided Berkovich indents in Pt<sub>57.5</sub>Cu<sub>14.7</sub>Ni<sub>5.3</sub>P<sub>22.5</sub> at annealing temperatures of 523K (250°C) and 513K (240°C). This indicates that the value of the surface tension  $\gamma = 0.19$  N/m over this 30 degree temperature range may be considered to be essentially constant.

## 5.4 Scaling considerations for the shape-recovery process

The relevant physical quantities related to the shape-recovery response at a *fixed* temperature include characteristic initial and final geometrical "length" scales associated with the microstructural features, the material properties, and the annealing time t. The relevant material properties are the Newtonian viscosity  $\eta$  and the surface tension  $\gamma$  at the given temperature. For microstructural features such as pyramidal protrusions or Berkovich indents, in which the initial and recovering protrusions (indents) are geometrically self-similar, the characteristic dimensions are the initial and evolving heights (depths)  $h_0$  and h, respectively.<sup>10</sup> For such problems the relevant physical parameters are

$$(h_0, h, \eta, \gamma, t)$$
.

From these five quantities it is possible to form two dimensionless groups,

$$\frac{h}{h_0}$$
 and  $\frac{\gamma t}{\eta h_0}$ , (5.5)

and presume that the recovery response scales as

$$\frac{h}{h_0} = F\left(\frac{\gamma t}{\eta h_0}\right),\tag{5.6}$$

where the function F is the shape-recovery response function for a given pyramidal geometry.

In order to evaluate whether this scaling argument holds, we plot in Figure 9(a) the shape-recovery data of Kumar and Schroers (2008) for the four-sided pyramidal protrusions of three initial heights annealed at 543 K, along with our corresponding simulations (shown as dashed lines), in the normalized coordinates (5.5). In plotting these results we used  $\eta(\vartheta = 543 \text{ K}) = 1.02 \times 10^7 \text{ Pa-s}$ ,  $\gamma = 0.19 \text{ N/m}$ , and the appropriate values for  $h_0$ . The experimental data and numerical simulation results essentially collapse to a single trend-line, confirming our scaling argument.<sup>11</sup>

Figure 9(b) shows the the recovery data of Packard et al. (2009) for the three-sided Berkovich indents of three initial heights annealed at 523 K or 513 K, along with the corresponding simulations. In plotting these results we used  $\eta(\vartheta = 523 \text{ K}) = 2.78 \times 10^8 \text{ Pa-s}, \ \eta(\vartheta = 513 \text{ K}) = 2.21 \times 10^9 \text{ Pa-s}, \ \gamma = 0.19 \text{ N/m}, \text{ and the}$ 

 $<sup>^{8}</sup>$ The simulations and the experimental data differ at the longest annealing times at 523 K.; this is likely due to the experimental difficulties in measuring feature depths below 100 nm at elevated temperatures.

 $<sup>^{9}</sup>$ The color scale bars in Figure 8(a) and (b) are not exactly the same, but are close enough to allow for a qualitative comparison between the simulations and the experiments.

<sup>&</sup>lt;sup>10</sup>To fully specify the geometry, additional dimensionless quantities are needed, such as the included angle for a conical or pyramidal geometry.

<sup>&</sup>lt;sup>11</sup>The small differences in the numerically calculated curves may be attributed to different values of the normalized time step  $\gamma \Delta t/\eta h_0$  used in the different simulations.

appropriate values for  $h_0$ . As in Figure 9(a) for the pyramidal protrusions, a similar reduction to a single trend-line is observed here for the recovery of the Berkovich indents.

Thus, if the shape-recovery response F for a given self-similar geometric feature is calculated or measured, the recovery for another initial geometry or recovery at another temperature my be estimated, as long as the surface tension and the Newtonian viscosity as a function of temperature is known.<sup>12</sup>

## 6 Concluding remarks

By integrating (i) a reasonably simple elastic-viscoplasticity theory for metallic glasses in the supercooled liquid state above the glass transition temperature, and (ii) a new methodology to numerically account for surface-tension effects, we have developed a computational capability which when coupled with (a) a knowledge of the elastic-viscoplastic response of the bulk glass from compression experiments, and (b) shape-recovery experiments of micro/nanoscale surface features on the metallic glass in its supercooled liquid region, may be used to *determine* the surface tension of the glass at the temperature at which the recovery experiment is conducted. We have demonstrated the use of this procedure to determine that the surface tension of Pt<sub>57.5</sub>Cu<sub>14.7</sub>Ni<sub>5.3</sub>P<sub>22.5</sub> at 543 K (270°C) is  $\gamma = 0.19$  N/m, and we have shown that this value of  $\gamma$  may be considered to be essentially constant over a temperature range of 30 degrees from 543 K to 513K.

The numerical simulation capability presented in this paper provides a basis for further simulationbased studies of surface tension-driven shape-recovery of arbitrarily shaped micro/nano-dimensioned surface features (not just pyramidal protrusions or intrusions!) on metallic glasses in the supercooled liquid region. Also, in conjunction with hot-nanoindentation, the phenomenon of surface tension-driven shape-recovery may prove to be an attractive basis for ultrahigh density re-writable data storage.

#### Acknowledgements

Financial support was provided by grants from NSF (CMS-0555614) and the Singapore-MIT Alliance (MST). Discussions with Dr. Corinne Packard and Professor Chris Schuh as well as access to their shape-recovery data is gratefully acknowledged.

## References

Abaqus. Reference manuals; 2008.

- Eleftheriou, E., Antonakopoulos, T., Binnig, G.K., Cherubini, G., Despont, M., Dholakia, A., Dürig, U., Lantz, M.A., Pozidis, H., Rothuizen, H.E., Vettiger, P., 2003. Millipede – A MEMS-Based Scanning-Probe Data-Storage System. IEEE Transactions on Magnetics 39, 938-945.
- Fulcher, G.S., 1925. Analysis of recent measurements of the viscosity of glasses. Journal of the American Ceramic Society 8, 339-355.
- Harmon, J.S., Demetriou, M.D., Johnson, W.L., 2007. Rheology and ultrasonic properties of Pt<sub>57.5</sub>Ni<sub>5.3</sub>Cu<sub>14.7</sub>P<sub>22.5</sub> liquid. Applied Physics Letters 90, 171923.
- Henann, D., Anand, L., 2008. A consitutive theory for the mechanical response of amorphous metals at high temperatures spanning the glass transition temperature: Application to microscale thermoplastic forming. Acta Materialia 56, 3290-3305.
- Henann, D.L., Srivastava, V., Taylor, H.K., Hale, M.R., Hardt, D.E., Anand, L., 2009. Metallic glasses: viable tool materials for the production of surface microstructures in amorphous polymers by micro-hotembossing. Journal of Micromechanics and Microengineering 19, 115030.
- Kumar, G., Schroers, J., 2008. Write and erase mechanisms for bulk metallic glass. Applied Physics Letters 92, 031901

 $<sup>^{12}</sup>$ Particular scaling functions F for Vickers pyramids and Berkovich indents may be sought by non-linear curve-fitting of the data in Figure 9(a,b); however, we refrain from doing so here.

Kumar, G., Tang, H.X., Schroers, J., 2009. Nanomoulding with amorphous metals. Nature 457, 868-872.

- Packard, C.E., Schroers, J., Schuh, C.A., 2009. In situ measurements of surface tension-driven shape-recovery in a metallic glass. Scripta Materialia 60, 1145-1148.
- Pozidis, H., Häberle, W., Wiesmann, D., Drechsler, U., Despont, M., Albrecht, T.R., Eleftheriou, E., 2004. Demonstration of Thermomechanical Recording at 641 Gbit/in<sup>2</sup>. IEEE Transaction on Magnetics 40, 2531-2536.
- Saksono, P.H., Perić, D., 2006. On finite element modelling of surface tension Variational formulation and applications – Part I: Quasistatic problems. Computational Mechanics 38, 265-281.
- Spaepen, F., 1977. A microscopic mechanism for steady state inhomogeneous flow in metallic glasses. Acta Metallurgica 25, 407-415.
- Tammann, V.G., Hesse, W., 1926. Die abhängigkeit der viscosität von der temperatur bei unterkühlten flüssigkeiten. Zeitschrift für anorganische und allgemeine Chemie 156, 245-257.
- Vettiger, P., Cross, G., Despont, M., Drechsler, U., Dürig, U., Gotsmann, B., Häberle, W., Lantz, M.A., Rothuizen, H.E., Stutz, R., Binnig, G.K., 2002. The "Millipede" – Nanotechnology Entering Data Storage. IEEE Transactions on Nanotechnology 1, 39-55.
- Vogel, H., 1921. Das temperaturabhängigkeitsgesetz der viskosität von flüssigkeiten. Physikalische Zeitschrift 22, 645-646.

## 7 Appendix: A method for calculating surface curvature

Recall from Section 5.1 that the surface tension boundary condition is equivalent to an externally-applied traction of the form

$$\mathbf{Tn} = -2\gamma\kappa\mathbf{n} \qquad \text{upon} \qquad \mathcal{S}_t, \tag{7.1}$$

where  $\gamma$  is the surface tension,  $\kappa$  is the mean curvature, and **n** is the outward unit normal to  $S_t$ . This traction boundary condition is applied through a user-subroutine DLOAD in Abaqus/Standard that allows for userdefined distributed loads, i.e. normal tractions. In this appendix, we focus attention on the calculation of the mean curvature  $\kappa$ .<sup>13</sup>

The DLOAD subroutine is called at each *load integration point* located on the free surface, for each iteration in a given time increment. Load integration points are distinct from material integration points. Material integration points are used to calculate the stiffness matrix for a given element in a finite element calculation, and it is at these points that quantities such as the stress and strain are calculated. Analogously, load integration points are used calculate the external force array for a given finite element located on the free surface, and likewise, it is at these points that the applied surface tractions are calculated. In our discussion when we use the term "integration point," we refer to load integration points, and not material integration points.

In the DLOAD subroutine, only the coordinates of the integration point are available, and data for the neighboring integration points are unavailable. However, in order to calculate the mean curvature at an integration point, the coordinates of the integration points surrounding that point are needed. We obtain this data by using the following strategy: we utilize a FORTRAN module which is available globally during the analysis. During each time increment, the current coordinates of all integration points are stored in the global module. Also the integration points nearest to each integration point are determined and stored in an array in the global module, and a global variable is used as a counter to determine the total number of load integration points processed in each time increment. At the beginning of a new time increment, the coordinates of each integration point and its nearest neighbors (stored from the previous step) are used to calculate the mean curvature at that point, and these values are stored in the global module and used to

 $<sup>^{13}</sup>$ Saksono and Perić (2006) have recently developed and implemented a finite element program in which they incorporate surface tension effects based on a weak form of equation (7.1). Here, for ease of implementation in a commercial finite element program, we apply equation (7.1) directly as a boundary condition.

determine the surface tension-related traction boundary condition at that integration point. For subsequent iterations in a given time increment, the mean curvatures calculated from the previous time increment are utilized. Thus, while the overall calculation is implicit, the application of the surface tension boundary conditions is explicit, with the load in a given time increment calculated using the mean curvature from the previous time increment. One must keep this in mind when choosing a time step for simulations, and as such, it was verified that the time step was small enough in the simulations presented in Section 5.

To demonstrate how the mean curvature is calculated at a given load integration point, we first consider the two-dimensional case, and then extend our methodology to three-dimensions. Consider the case of a free surface in a two-dimensional, plane-strain simulation, which uses four-node reduced integration elements. In this case each element possesses a single load integration point; cf. Figure 10(a). Nodes are denoted by a filled, black circle, and the load integration points are denoted by an X; the coordinates of the integration points are given in terms of the global coordinate system Oxy. To calculate the mean curvature at the center integration point A, we fit a parabola through the point A and its two nearest neighbors, B and C, and use the resulting fit to calculate the mean curvature at A. However, when fitting a parabola through three discrete points, the resulting parabola, and hence the calculated mean curvature, is highly dependent on the orientation of the coordinate system used. Thus, we choose to calculate the mean curvature at A in the coordinate frame with origin located at A and y-axis aligned with the local surface normal **n**, shown as Ax'y' in Figure 10(a). The local surface normal is calculated as the normal vector to the line passing through the two nearest neighbor points B and C, denoted by the dotted line in Figure 10(a).<sup>14</sup> In general, the form for a parabolic fitting function is  $y' = ax'^2 + bx' + c$ ; however, in using a local coordinate system with origin at the point A and y-axis aligned with the local surface of the fitting through the two nearest neighbor points B and C, denoted by the dotted line in Figure 10(a).<sup>14</sup> In general, the form for a parabolic fitting function is  $y' = ax'^2 + bx' + c$ ; however, in using a local coordinate system with origin at the point A and y-axis aligned with the local surface normal, the first derivative of the fitting

function, as well as the value of function itself, should be zero at the point  $(y' = \frac{dy'}{dx'} = 0 \text{ at } x' = 0)$ . Thus, we force b = c = 0 and take the fitting function to be in the form  $y' = ax'^2$ . The resulting mean curvature is  $\kappa = -\frac{1}{2}\frac{\partial^2 y'}{\partial x'^2} = -a$ .

In summary, in a two-dimensional, plane-strain setting, given the global coordinates of the integration point A,  $(x_0, y_0)$ , and the coordinates of the two nearest neighbors B and C,  $(x_1, y_1)$  and  $(x_2, y_2)$ , the mean curvature at A is calculated as follows:

1. Calculate the components of the local outward surface normal  $\mathbf{n} = n_x \mathbf{e}_x + n_y \mathbf{e}_y$  in the global coordinate system from the coordinates of the two nearest neighbor points:

$$n_x = \frac{-(y_2 - y_1)}{\sqrt{(y_2 - y_1)^2 + (x_2 - x_1)^2}}, \qquad n_y = \frac{(x_2 - x_1)}{\sqrt{(y_2 - y_1)^2 + (x_2 - x_1)^2}}.$$
(7.2)

2. Calculate the rotation matrix relating the primed (local) and unprimed (global) coordinate systems:

$$[\mathbf{Q}] = \begin{bmatrix} n_y & -n_x \\ n_x & n_y \end{bmatrix}.$$
(7.3)

3. Calculate the coordinates of the nearest neighbors in the primed (local) coordinate system:

$$\begin{bmatrix} x_1'\\ y_1' \end{bmatrix} = [\mathbf{Q}] \begin{bmatrix} x_1 - x_0\\ y_1 - y_0 \end{bmatrix},$$
  
$$\begin{bmatrix} x_2'\\ y_2' \end{bmatrix} = [\mathbf{Q}] \begin{bmatrix} x_2 - x_0\\ y_2 - y_0 \end{bmatrix}.$$
(7.4)

4. Fit a parabola of the form

$$y' = ax'^2 \tag{7.5}$$

to the points by performing a linear least squares fit to the system of equations

$$\begin{bmatrix} y_1'\\ y_2' \end{bmatrix} = a \begin{bmatrix} x_1'^2\\ x_2'^2 \end{bmatrix}, \tag{7.6}$$

 $<sup>^{14}</sup>$ Note that the normal vector is determined up to its sign. Thus, some knowledge of orientation of the free surface is necessary to ensure that the normal vector **n** is the outward-facing surface normal and not incorrectly inward-facing.

which yields

$$a = \frac{x_1'^2 y_1' + x_2'^2 y_2'}{x_1'^4 + x_2'^4}.$$
(7.7)

5. The mean curvature is then given by  $^{15}$ 

$$\kappa = -\frac{1}{2} \frac{\partial^2 y'}{\partial x'^2} = -a. \tag{7.9}$$

The procedure to calculate the mean curvature in three-dimensions is analogous but slightly more complex. In a three-dimensional simulation which uses eight-node, fully-integrated elements (as used in Section 5), there are four load integration points per surface element. A schematic of a free surface in a threedimensional setting is shown in Figure 10(b); nodes are denoted by a filled, black circle, and integration points are denoted by an X. To calculate the mean curvature at the point A in this case, we fit a paraboloid through A (with global coordinates  $(x_0, y_0)$ ) and its *eight* nearest neighbors (enumerated 1-8 in Figure 10(b) and with global coordinates  $(x_i, y_i)$  for i = 1, 8) and use the resulting fit to calculate the mean curvature at A. The details of the procedure are described below:

1. Calculate the components of the local outward surface normal  $\mathbf{n} = n_x \mathbf{e}_x + n_y \mathbf{e}_y + n_z \mathbf{e}_z$  in the global coordinate system. This is done by first fitting a plane of the form z = ax + by + c to the *eight* nearest neighbors. The local surface normal is then calculated as the normal vector to this plane. Its components are given by<sup>16</sup>

$$n_x = \frac{-a}{\sqrt{a^2 + b^2 + 1}}, \qquad n_y = \frac{-b}{\sqrt{a^2 + b^2 + 1}}, \qquad n_z = \frac{1}{\sqrt{a^2 + b^2 + 1}}.$$
 (7.10)

2. Calculate the rotation matrix relating the primed (local) and unprimed (global) coordinate systems:<sup>17</sup>

$$\left[\mathbf{Q}\right] = \begin{bmatrix} \frac{(n_x^2 n_z + n_y^2)}{n_x^2 + n_y^2} & \frac{-n_x n_y (1 - n_z)}{n_x^2 + n_y^2} & -n_x \\ \frac{-n_x n_y (1 - n_z)}{n_x^2 + n_y^2} & \frac{(n_x^2 + n_y^2 n_z)}{n_x^2 + n_y^2} & -n_y \\ n_x & n_y & n_z \end{bmatrix}.$$
 (7.11)

3. Calculate the coordinates of the nearest neighbors in the primed coordinate system:

$$\begin{bmatrix} x'_i \\ y'_i \\ z'_i \end{bmatrix} = [\mathbf{Q}] \begin{bmatrix} x_i - x_0 \\ y_i - y_0 \\ z_i - z_0 \end{bmatrix} \quad \text{for } i = 1, 8 \text{ (eight nearest points)}.$$
(7.12)

4. Fit a paraboloid of the form<sup>18</sup>

$$z' = ax'^2 + by'^2 + cx'y'$$
(7.13)

٦

<sup>15</sup>In an axisymmetric setting, the mean curvature is given as

$$\kappa = \frac{1}{2} \left[ -\frac{\partial^2 y'}{\partial x'^2} + \frac{-\left(\frac{n_x}{n_y}\right)}{r\left(1 + \left(-\frac{n_x}{n_y}\right)^2\right)^{1/2} \operatorname{sign}(n_y)} \right],\tag{7.8}$$

where r is the distance from the point to the axis of revolution. The first term is due to the in-plane curvature and the second term is due to the out-of-plane curvature.

 $^{16}$ As in the two-dimensional case, the normal vector is determined up to its sign, and care must be taken to ensure **n** is outward-facing.

<sup>17</sup>This rather complicated rotation matrix represents a rotation of the coordinate axes about the unit vector  $\frac{(\mathbf{e}_z \times \mathbf{n})}{|\mathbf{e}_z \times \mathbf{n}|}$  aligning  $\mathbf{e}'_z$  with  $\mathbf{n}$ .

 $z^{-18}$ As before, in using a local coordinate system with origin located at the point A and z-axis aligned with the local surface normal, the first derivatives of the fitting function, as well as the value of function itself, should be zero at the point. Therefore, these terms are left out of the fitting function.

to the points by performing a linear least squares to the system of equations

$$z'_{i} = ax'_{i}{}^{2} + by'_{i}{}^{2} + cx'_{i}y'_{i}$$
 for  $i = 1, 8$  (eight nearest points). (7.14)

Hence, from the eight neighboring points, we get eight equations for the three unknowns (a, b, c). With [d] denoting a  $3 \times 1$  matrix for the three unknowns (a, b, c) as its components, [z] denoting a  $8 \times 1$  matrix with the eight  $z'_i$  values as its components, and [A] a  $8 \times 3$  matrix with corresponding  $(x'_i^2, y'_i^2, x'_i y'_i)$  values in each row, the system of equations for determining [d] may be written in matrix form as

$$[A][d] = [z]. (7.15)$$

An optimal solution for this over-determined system is obtained through a linear least-squares fit by using a standard result from linear algebra:

$$[d] = ([A]^{\top}[A])^{-1}[A]^{\top}[z].$$
(7.16)

5. The mean curvature is then given by

$$\kappa = -\frac{1}{2} \left( \frac{\partial^2 z'}{\partial x'^2} + \frac{\partial^2 z'}{\partial y'^2} \right) = -(a+b).$$
(7.17)

The above procedure was implemented in a DLOAD user-subroutine in Abaqus/Standard. It was verified in finite element simulations using the DLOAD that the correct internal pressure was obtained for simple geometries such as a sphere and a long cylinder. The DLOAD was then used in the simulations reported in Section 5.



Figure 1: SEM micrographs of pyramidal microfeatures of two different initial heights ( $\approx 5 \,\mu$ m and  $\approx 2 \,\mu$ m) after annealing at 543 K (270°C) for 60, 300, and 1200 s. From Kumar and Schroers (2008).



Figure 2: Viscosity (a) as a function of strain rate at various temperatures, and (b) as a function of temperature for several selected strain rates. Points are data from Harmon et al. (2007); lines are the model prediction.



Figure 3: Initial finite element mesh configuration for the simulations of the shape-recovery of raised pyramidal microfeatures: (a) a three-dimensional perspective view, and (b) a two-dimensional projection of the side view of the domain.



Figure 4: Feature height h as a function of annealing time at 543 K (270°C) for the pyramidal microfeatures of three different initial heights. The symbols are experimental data from Kumar and Schroers (2008), and the dashed lines are the results from our numerical simulations.



Figure 5: (a) SEM micrographs (from Kumar and Schroers (2008)) and (b) corresponding numerical predictions of the largest pyramidal feature ( $h_0 = 4.67 \,\mu\text{m}$ ) after annealing at 543 K (270°C) for 60, 300, and 1200 s.



Figure 6: Initial finite element mesh configuration for the simulations of the shape-recovery of residual Berkovich indents, including (a) a three-dimensional perspective view and (b) a two-dimensional projection of the side view of the domain.



Figure 7: Residual indent depth h as a function of annealing time for residual Berkovich indents annealed (a) 523 K (250°C) and (b) 513 K (240°C). The symbols are experimental data from Packard et al. (2009), and the dashed lines are the results from our simulations.



Figure 8: (a) Experimentally-measured topographic contour plots (from Packard et al. (2009)) and (b) corresponding simulated contour plots of the largest residual Berkovich indent ( $h_0 = 264 \text{ nm}$ ) after annealing at 523 K (250°C) for 20, 40 and 60 minutes.



Figure 9: Normalized feature height  $h/h_0$  as a function of normalized annealing time  $\gamma t/\eta h_0$  for (a) pyramidal microfeatures annealed at 543 K and (b) residual Berkovich indents annealed 523 K and 513 K. The results from the numerical simulations are shown as dashed lines.



Figure 10: (a) Schematic of a free surface in a two-dimensional, plane-strain setting, using four-node reducedintegration elements. (b) Schematic of a free surface in a three-dimensional setting, using eight-node fullyintegrated elements. Nodes are denoted by a filled, black circle, and load integration points are denoted by an X.