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# The influence of surface mechanics on diffusion induced stresses within spherical nanoparticles

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We examine the effects of surface tension and surface modulus on diffusion-induced stresses within spherical nanoparticles. We show that both the magnitude and distribution of stresses can be significantly affected by surface mechanics if the particle diameter is in the nanometer range. In particular, a tensile state of stress may be significantly reduced in magnitude or even be reverted to a state of compressive stress with decreasing particle radius. This reduction in tensile stress may be responsible for the observed resilience to fracture and decrepitation of nanoparticles used in various industrial applications. © 2008 American Institute of Physics. [DOI: 10.1063/1.3000442]

## I. INTRODUCTION

Stresses can occur as a result of compositional inhomogeneities during solid-state diffusion. The ubiquitous nature of diffusion-induced stresses (DISs) is evident in many technological areas, including dopant diffusion in semiconductor processing, oxidation of metals, hydrogen transport in solid-state hydrogen-storage media, and lithium diffusion in battery electrodes. A number of authors have developed models for DIS. For example, Prussin<sup>1</sup> made an analogy between thermal stress and DIS and analyzed the transverse stresses developed in a thin plate during mass transfer. Li<sup>2</sup> provided a number of analytical solutions to DIS problems in spherical, cylindrical, and thin plate geometry. Lee and co-workers<sup>3–5</sup> also studied DIS in various systems including thin plates, hollow cylinders, and composites. Yang and Li<sup>6</sup> considered the effect of DISs on the bending of beam and plate structures for sensing applications. Yang also studied the coupled problem of interactions of stress and diffusion.<sup>7</sup> Recently, Christensen and Newman<sup>8</sup> and Zhang *et al.*<sup>9</sup> studied stresses generated during Li diffusion in lithium battery electrodes.

Diffusion in nanostructured materials has become, in recent years, the cornerstone of many technological developments. In metal hydride and lithium battery research, for example, it is known that stresses induced by hydrogen or lithium diffusion, respectively, can lead to fracture and decrepitation of electrode materials, which limit the durability of batteries.<sup>10–12</sup> Nanostructured battery electrodes,<sup>13–20</sup> such as thin films, nanoparticles, and nanowires, have often been shown to have substantially longer durability in terms of cycle life than their bulk counterparts. It is therefore important to clarify phenomena associated with DISs in nanostructures, such as spherical particles.

With decreasing particle size, the effect of the surface is expected to become more significant since the ratio of surface to volume quantities scales as the inverse of the particle

size. In particular, surface energy and surface stress are expected to affect the magnitude and distribution of DISs when the radius of the particle is at the nanometer scale. In this paper, we provide an analytical model for DIS in nanospheres by taking into account the effect of the surface energy and surface stress.

## II. ANALYTICAL MODEL, RESULTS, AND DISCUSSION

The concept of surface energy and surface stress originates from the work of Gibbs.<sup>21</sup> The expression for the surface stress tensor,  $\sigma_{\alpha\beta}^{\text{surf}}$ , is usually written as (see recent reviews in Refs. 21–25)

$$\sigma_{\alpha\beta}^{\text{surf}} = \gamma \delta_{\alpha\beta} + \frac{\partial \gamma}{\partial \varepsilon_{\alpha\beta}}, \quad (1)$$

where  $\gamma$  is surface energy per unit area,  $\varepsilon_{\alpha\beta}$  is a  $2 \times 2$  surface strain tensor, and  $\delta_{\alpha\beta}$  is the Kronecker delta function. Equation (1) is known as the Shuttleworth formula.<sup>22,26</sup> For liquids, surface stress and  $\gamma$  have the same value because of the high mobility of atoms in fluids, which facilitates the transfer of atoms to the surface and therefore keeps  $\gamma$  constant when surface area changes [i.e.,  $(\partial \gamma / \partial \varepsilon_{\alpha\beta}) = 0$ ]. For solids, surface stress and surface energy are not the same because of the finite elasticity of solid surfaces.

A general theory for surface elasticity has been developed by Gurtin and co-workers<sup>27–29</sup> and is the basis for many recent studies of surface effects on the micromechanical behavior of solids. For isotropic spherical particles deforming uniformly, the surface strains, in the spherical coordinate system, along any two perpendicular directions are principal strains of equal magnitude, i.e.,  $\varepsilon_{\theta} \equiv \varepsilon_{\theta\theta} = \varepsilon_{\phi\phi}$ . As a result, the surface constitutive relation for the surface stress may be written as:<sup>30</sup>

$$\sigma_{\theta}^{\text{surf}} = \sigma_{\theta\theta}^{\text{surf}} = \sigma_{\phi\phi}^{\text{surf}} = \tau^0 + K^s \varepsilon_{\theta}, \quad (2)$$

where  $\tau^0$  is the deformation-independent surface tension and  $K^s$  is the “surface modulus.”<sup>30,31</sup> Equation (2) may also be considered as an application of the linear-elastic surface constitutive model of Miller and Shenoy [Eqs. (7) and (8) in Ref. 31] to the present case of isotropic spherical particles.

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The bulk of the spherical particle is assumed to be an isotropic linear-elastic solid. Using the analogy between thermal and DIS,<sup>1-7</sup> one can state the stress-strain relationships in the spherical coordinate system as

$$\begin{aligned}\varepsilon_r &= \frac{1}{E}(\sigma_r - 2\nu\sigma_\theta) + \frac{1}{3}\Omega C, \\ \varepsilon_\theta &= \frac{1}{E}[(1-\nu)\sigma_\theta - \nu\sigma_r] + \frac{1}{3}\Omega C,\end{aligned}\quad (3)$$

where  $E$  is Young's modulus,  $\nu$  is Poisson's ratio,  $C$  is molar concentration, and  $\Omega$  is the partial molar volume of the solute. We further assume that the elastic properties are independent of the concentration  $C$ .

Because of spherical symmetry, the radial and tangential strains, in the infinitesimal formulation of deformation, can be expressed as functions of radial displacement,  $u$ , as:<sup>32</sup>

$$\varepsilon_r = \frac{du}{dr} \quad \text{and} \quad \varepsilon_\theta = \frac{u}{r}. \quad (4)$$

Since atomic diffusion in solids is a much slower process than elastic deformation, mechanical equilibrium is established much faster than that of diffusion. Mechanical equilibrium is, therefore, treated as a static equilibrium problem. In the absence of any body force, the equation for static mechanical equilibrium in the bulk of a sphere is given by:<sup>32</sup>

$$\frac{d\sigma_r}{dr} + 2\frac{\sigma_r - \sigma_\theta}{r} = 0. \quad (5)$$

Substituting Eqs. (3) and (4) into Eq. (5), we obtain a second order ordinary differential equation for the displacement,<sup>32</sup>

$$\frac{d^2u}{dr^2} + \frac{2}{r}\frac{du}{dr} - \frac{2u}{r^2} = \left(\frac{1+\nu}{1-\nu}\right)\frac{\Omega}{3}\frac{dC}{dr}. \quad (6)$$

Integrating this equation with respect to  $r$  yields an analytical solution for  $u$  with two integration constants. These two constants are determined by the requirements that (1) the displacement at the center of the sphere is zero and (2) the radial stress,  $\sigma_r$ , must satisfy mechanical equilibrium at the surface of the spherical particle. The condition for equilibrium at the surface is given by<sup>30</sup>

$$\sigma_r(r \rightarrow R) = -\frac{2\sigma_\theta^{\text{surf}}}{R}, \quad (7)$$

where  $R$  is the radius of the spherical particle. For large particles,  $\sigma_\theta^{\text{surf}}/R \rightarrow 0$ , which is the conventional boundary condition at free surfaces,  $\sigma_r=0$ .

We obtain the solutions for the normal and tangential stresses that satisfy the boundary condition Eq. (7) and remain finite at  $r=0$ ;

$$\begin{aligned}\sigma_r(r) &= \frac{2E\Omega}{9(1-\nu)} \left[ \left( \frac{1 - \frac{K^s(1+\nu)}{R} \frac{E}{E}}{1 + \frac{2K^s(1-2\nu)}{R} \frac{E}{E}} \right) C_{\text{av}}(R) - C_{\text{av}}(r) \right] \\ &\quad - \frac{\frac{2\tau^0}{R}}{1 + \frac{2K^s(1-2\nu)}{R} \frac{E}{E}}, \\ \sigma_\theta(r) &= \frac{E\Omega}{9(1-\nu)} \\ &\quad \times \left[ 2 \left( \frac{1 - \frac{K^s(1+\nu)}{R} \frac{E}{E}}{1 + \frac{2K^s(1-2\nu)}{R} \frac{E}{E}} \right) C_{\text{av}}(R) + C_{\text{av}}(r) - 3C(r) \right] \\ &\quad - \frac{\frac{2\tau^0}{R}}{1 + \frac{2K^s(1-2\nu)}{R} \frac{E}{E}},\end{aligned}\quad (8)$$

where  $C_{\text{av}}(r) \equiv (3/r^3) \int_0^r r'^2 C(r') dr'$  is the average concentration in the spherical volume of radius  $r$  within the particle of radius  $R$ . These equations reduce to the well-known expressions for normal and tangential stresses when the size of the particles is large so that the surface energy and surface stress terms can be ignored:<sup>2</sup>

$$\begin{aligned}\sigma_r(r) &= \frac{2E\Omega}{9(1-\nu)} [C_{\text{av}}(R) - C_{\text{av}}(r)], \\ \sigma_\theta(r) &= \frac{E\Omega}{9(1-\nu)} [2C_{\text{av}}(R) + C_{\text{av}}(r) - 3C(r)].\end{aligned}\quad (9)$$

However, when the radius of the spherical particles is small, surface effects become important.

The radial and tangential stresses can be obtained from Eq. (8) once the concentration profile  $C(r)$  is known at any given time  $t$ . Although the concentration profile  $C(r, t)$  can be obtained by solving an appropriate diffusion problem, several general statements can be made that are independent of the details of the diffusional processes. Specifically, we consider the "mean" stress defined as  $\sigma(r) = [\sigma_r(r) + \sigma_\theta(r) + \sigma_\phi(r)]/3$ . Since  $\sigma_\theta(r) = \sigma_\phi(r)$ , the mean stress becomes

$$\begin{aligned}\sigma(r) &= \frac{\sigma_r(r) + 2\sigma_\theta(r)}{3} \\ &= \frac{2E\Omega}{9(1-\nu)} \left[ \left( \frac{1 - \frac{K^s(1+\nu)}{R} \frac{E}{E}}{1 + \frac{2K^s(1-2\nu)}{R} \frac{E}{E}} \right) C_{\text{av}}(R) - C(r) \right] \\ &\quad - \frac{\frac{2\tau^0}{R}}{1 + \frac{2K^s(1-2\nu)}{R} \frac{E}{E}}.\end{aligned}\quad (10)$$

Thus, both surface tension and surface stress have an effect on the mean stress when the diameter of the particle is sufficiently small. Since  $\lim_{r \rightarrow 0} C_{av}(r) = C(0)$ , Eqs. (8) and (9) show that the stress state at the center of the sphere is purely hydrostatic, i.e.,  $\lim_{r \rightarrow 0} \sigma_r(r) = \lim_{r \rightarrow 0} \sigma_\theta(r)$ , with or without the influence of surface energy and surface stress. Thus, surface energy and stress can alter the magnitude of the mean stress at the center, while keeping the stress state purely hydrostatic.

Because of the spherical symmetry, one principal shear stress is zero and the other two are both equal to  $(\sigma_r - \sigma_\theta)/2$ . Equation (8) shows that the principal shear stress is  $[\sigma_r(r) - \sigma_\theta(r)]/2 = E\Omega[C(r) - C_{av}(r)]/6(1 - \nu)$ . Thus, surface energy and surface stress do not have any effect on the magnitude and distribution of principal shear stresses for any size particles. As a result, surface energy and surface stress do not affect the von Mises stress distribution either. They do, however, affect the magnitude and distribution of radial, tangential, and hydrostatic stresses through two factors,

$$S_1 = \frac{1 - \frac{K^s(1 + \nu)}{R} \frac{E}{E}}{1 + \frac{2K^s(1 - 2\nu)}{R} \frac{E}{E}} \quad \text{and} \quad S_2 = -\frac{\frac{2\tau^0}{R}}{1 + \frac{2K^s(1 - 2\nu)}{R} \frac{E}{E}}. \quad (11)$$

In general, at any given time, the effect of  $K^s$  is depth independent since  $K^s$  enters Eq. (8) through  $S_1 C_{av}(R)$ , which is depth independent. The  $K^s$  effect is, however, time dependent since  $C_{av}(R)$  is a function of time. In contrast, the surface tension,  $\tau^0$ , contributes to a time-independent constant compressive stress to both the radial and tangential stresses through the term  $S_2$ . The effect of  $S_2$  is independent of concentration. The parameter  $S_2$  has the dimension of stress and the negative sign ensures that this surface tension term contributes to a constant compressive stress to the radial, tangential, and hydrostatic stresses throughout the spherical particle. Taking a representative value of 1 J/m<sup>2</sup> for surface tension of metals,<sup>33</sup> we find that the magnitudes of the compressive stress due to  $2\tau^0/R$  alone are 2 GPa, 200 MPa, and 20 MPa for radii of 1, 10, and 100 nm, respectively. Thus, surface tension can have a strong effect on radial, tangential, and hydrostatic stresses when the diameter is less than a few tens of nanometers.

To further quantify the effects of surface energy and surface stress, we consider a simple problem of diffusion in a sphere of radius  $R$  with a constant diffusion coefficient,  $D$ , an initial constant concentration,  $C_0$ , and a constant surface concentration,  $C_R$ . The diffusion equation together with the initial and boundary conditions in the spherical coordinate system are given by<sup>34</sup>

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} D \frac{\partial C}{\partial r},$$

$$C(r, 0) = C_0, \quad \text{for } 0 \leq r \leq R,$$

$$C(R, t) = C_R, \quad \text{for } t \geq 0,$$

$$C(0, t) = \text{finite}, \quad \text{for } t \geq 0. \quad (12)$$

The analytic solution of the diffusion problem is well known and is reproduced here,<sup>34</sup>

$$\frac{C(r, t) - C_0}{C_R - C_0} = 1 + 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{n \pi (r/R)} \sin\left(\frac{n \pi r}{R}\right) e^{-n^2 \pi^2 D t / R^2}. \quad (13)$$

The average concentrations  $C_{av}(R)$  and  $C_{av}(r)$  are then given by

$$\begin{aligned} \frac{C_{av}(R) - C_0}{C_R - C_0} &= 1 - 6 \sum_{n=1}^{\infty} \frac{1}{n^2 \pi^2} e^{-n^2 \pi^2 D t / R^2}, \\ \frac{C_{av}(r) - C_0}{C_R - C_0} &= 1 + \frac{6R^3}{r^3} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^3 \pi^3} \\ &\quad \times \left( \sin \frac{n \pi r}{R} - \frac{n \pi r}{R} \cos \frac{n \pi r}{R} \right) e^{-n^2 \pi^2 D t / R^2}. \end{aligned} \quad (14)$$

Equations (13) and (14) can be substituted into Eq. (8) to obtain the solutions for stresses,

$$\begin{aligned} \frac{\sigma_r}{\left[ \frac{E\Omega(C_R - C_0)}{3(1 - \nu)} \right]} &= \frac{2}{3} (S_1 - 1) \left( \frac{C_R}{C_R - C_0} \right) - 4 \sum_{n=1}^{\infty} e^{-n^2 \pi^2 \tau} \\ &\quad \times \left[ \frac{S_1}{(n \pi)^2} + (-1)^n \left( \frac{\sin(n \pi x) - n \pi x \cos(n \pi x)}{(n \pi)^3} \right) \right] \\ &\quad + \frac{S_2}{\left[ \frac{E\Omega(C_R - C_0)}{3(1 - \nu)} \right]}, \\ \frac{\sigma_\theta}{\left[ \frac{E\Omega(C_R - C_0)}{3(1 - \nu)} \right]} &= \frac{2}{3} (S_1 - 1) \left( \frac{C_R}{C_R - C_0} \right) - 2 \sum_{n=1}^{\infty} e^{-n^2 \pi^2 \tau} \\ &\quad \times \left[ \frac{2S_1}{(n \pi)^2} + \frac{(-1)^n}{n \pi x} \sin(n \pi x) \right. \\ &\quad \left. - (-1)^n \left( \frac{\sin(n \pi x) - n \pi x \cos(n \pi x)}{(n \pi x)^3} \right) \right] \\ &\quad + \frac{S_2}{\left[ \frac{E\Omega(C_R - C_0)}{3(1 - \nu)} \right]}, \end{aligned} \quad (15)$$

where  $x = r/R$  and  $\tau = Dt/R^2$ .

Two cases of special interest are (1) “insertion” with initial condition  $C_0 = 0$  and a finite  $C_R$  and (2) “deinsertion”

with a finite  $C_0$  and  $C_R=0$ . When surface effects are absent (i.e.,  $S_1=1$  and  $S_2=0$ ), the normalized stresses during insertion,  $\sigma_r$  or  $\theta/[E\Omega C_R/3(1-\nu)]$ , and deinsertion,  $\sigma_r$  or  $\theta/[E\Omega C_0/3(1-\nu)]$ , have the same magnitude but opposite signs,

$$\begin{aligned} \frac{\sigma_r}{\left[\frac{E\Omega(C_R-C_0)}{3(1-\nu)}\right]} &= -4 \sum_{n=1}^{\infty} e^{-n^2 \pi^2 \tau} \left[ \frac{1}{(n\pi)^2} + (-1)^n \right. \\ &\quad \times \left. \left( \frac{\sin(n\pi x) - n\pi x \cos(n\pi x)}{(n\pi x)^3} \right) \right], \\ \frac{\sigma_\theta}{\left[\frac{E\Omega(C_R-C_0)}{3(1-\nu)}\right]} &= -2 \sum_{n=1}^{\infty} e^{-n^2 \pi^2 \tau} \left[ \frac{2}{(n\pi)^2} \right. \\ &\quad + \frac{(-1)^n}{n\pi x} \sin(n\pi x) - (-1)^n \\ &\quad \times \left. \left( \frac{\sin(n\pi x) - n\pi x \cos(n\pi x)}{(n\pi x)^3} \right) \right]. \end{aligned} \quad (16)$$

This “symmetry” is broken when surface effects become significant as seen from Eq. (15).

The results for insertion and deinsertion in the absence of surface effects are shown in Figs. 1 and 2. Figure 1 shows the concentration, radial, and tangential stresses as a function of position and time during insertion. The radial stress is tensile in the sphere. At a given time, the tensile radial stress is the highest at the center and decreases monotonically to zero at the surface. It can be shown<sup>32</sup> that the maximum radial stress at the center occurs when the dimensionless time,  $\tau=Dt/R^2 \approx 0.0574$ , which is just after the solute reaches the center of the sphere. The radial stress at the center then decreases with increasing concentration. The tangential stress is compressive at the surface and tensile at the center of the sphere. The tensile tangential stress at the center appears before the solute reaches there. At the center, the tangential and radial stresses always have the same magnitude so that the stress at the center is purely hydrostatic in tension. The maximum tangential stress, which is compressive, occurs at the surface at time zero. Opposite conclusions (i.e., replacing tension by compression) hold for deinsertion (see Fig. 2). The stress distribution is “size independent” in the sense that with proper scaling of the length and time scales (i.e.,  $x=r/R$  and  $\tau=Dt/R^2$ ) the stress distribution is identical for all particle radii (see Eq. (16) and Figs. 1 and 2).

In contrast, surface energy and surface stress can contribute to the “size effect” in stress distribution, i.e., the stress distribution for small particle radius is no longer the same as that for large radius. The magnitude of this size effect depends on the particle radius,  $R$ , and material properties,  $E$ ,  $\nu$ ,  $\tau^0$ ,  $K^s$ , and  $\Omega C_R$  (note: this dimensionless number can be considered as the volume expansion coefficient at the maximum concentration). For illustration purposes, we choose parameters  $E=10$  GPa,  $\nu=0.3$ , and  $\Omega C_R=0.08$  that were used

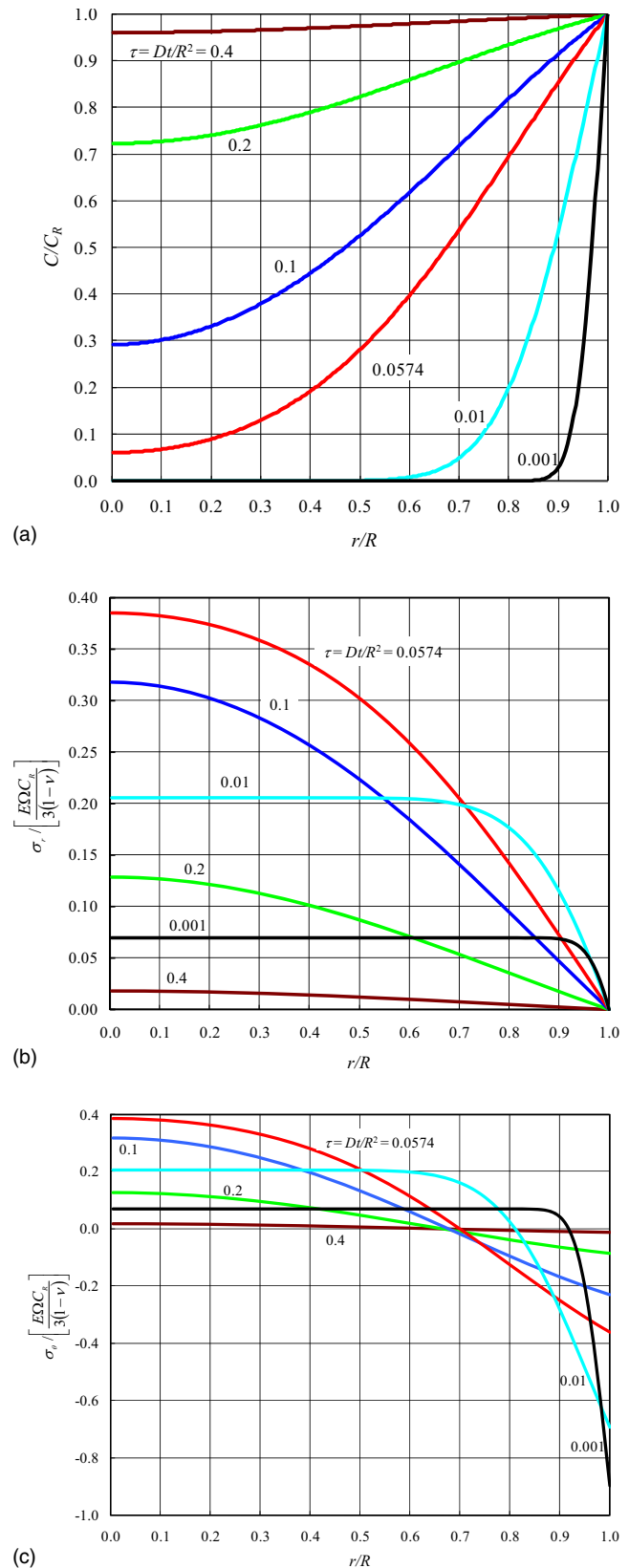


FIG. 1. (Color online) Concentration profile (a) and the corresponding radial stress (b) and tangential stress (c) without surface effects for insertion.

in a recent paper by Zhang *et al.*<sup>9</sup> for a Li-battery electrode material. Since the surface properties are unknown for this material, we take a representative value of  $1 \text{ J/m}^2$  for  $\tau^0$ .<sup>33</sup> Presently, the surface modulus values,  $K^s$ , have only been



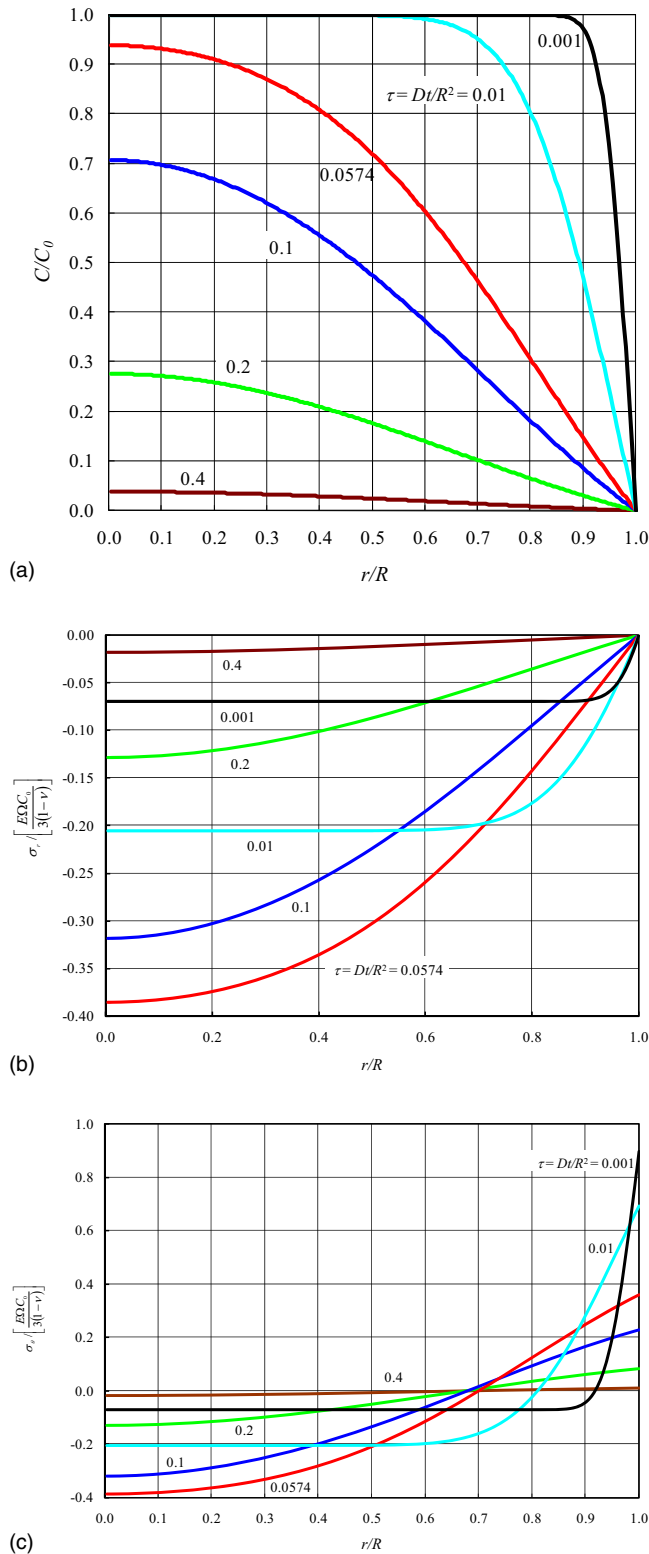


FIG. 2. (Color online) Concentration profile (a) and the corresponding radial stress (b) and tangential stress (c) without surface effects for deinsertion.

calculated for a few materials such as Al and Si.<sup>31</sup> Here, we use two values, +5 and -5 N/m for  $K^s$ , since (1) the surface modulus can be either positive or negative<sup>34</sup> and (2) the magnitude of 5 N/m is of the same order of magnitude as those calculated for Al and Si.

Figure 3 illustrates the effects of surface tension  $\tau^0$  and surface modulus  $K^s$  on the radial stress when the dimension-

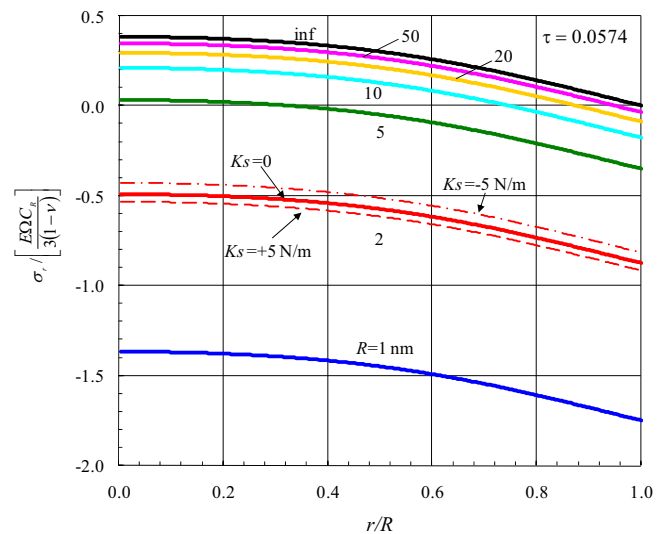


FIG. 3. (Color online) Effects of surface tension  $\tau^0$  and surface modulus  $K^s$  on radial stress during insertion at dimensionless time 0.0574 for spherical particles of various radii. The parameters used for the illustration are  $\tau^0 = 1$  J/m<sup>2</sup> and  $K^s = 0$  unless noted otherwise.

less time is at 0.0574 which corresponds to the maximum tensile stress at the center of the spherical particle during the entire insertion process. Figure 4 shows the effects of  $\tau^0$  and  $K^s$  on the tangential stress when the dimensionless time is at 0.001 during deinsertion when there is a very high tensile stress at the surface of the spherical particle. It is evident that the surface tension  $\tau^0$  and, to a lesser extent, surface modulus  $K^s$  becomes increasingly important with decreasing particle radius, making radial and tangential stresses less tensile and more compressive.

As an application of the above stress analysis, we consider fracture and decrepitation due to tensile stresses caused by composition inhomogeneities. Since surface tension and surface modulus can lower tensile stresses or even convert the state of stress from tensile to compressive, the tendency to fracture and decrepitate can be reduced with decreasing particle radius down to the nanometer range. Specifically, the radial tensile stress at the center during insertion and tangential tensile stress at the surface during de-insertion can be

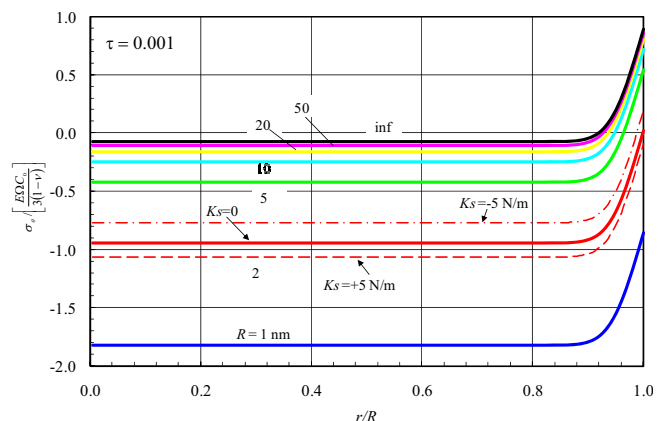


FIG. 4. (Color online) Effects of surface tension  $\tau^0$  and surface modulus  $K^s$  on tangential stress during deinsertion at dimensionless time 0.001 for spherical particles of various radii. The parameters used for the illustration are  $\tau^0 = 1$  J/m<sup>2</sup> and  $K^s = 0$  unless noted otherwise.

significantly reduced with decreasing particle radius. This surface energy and surface stress effect may therefore be one of the factors responsible for the observed resilience to fracture of nanoparticles used in metal hydride and lithium batteries. Furthermore, the stress analysis suggests remedies for avoiding fracture and decrepitation due to DIS. For example, materials with low volume expansion coefficient, low Young's modulus, high surface tension, and high positive surface modulus are expected to be able to sustain DIS, especially when the particle radius is in the nanometer range. Although we have analyzed DIS in a homogeneous spherical particle, the same results are applicable to thin and adherent coatings or surface modified layers on spherical particles where the surface mechanical properties may be engineered quite independently from the bulk properties, leading to a surface engineering approach to further reduce fracture and decrepitation tendencies of spherical particles for various applications.

### III. SUMMARY

We have analyzed DIS in spherical particles and showed that surface tension and surface stress may significantly affect the magnitude and distribution of radial, tangential, and mean stresses, but not shear stresses caused by composition inhomogeneities. We proposed that the tendency for fracture and decrepitation caused by tensile stresses could be reduced or avoided by reducing particle radius to nanometer range or by properly modifying the surface and bulk mechanical properties.

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<sup>1</sup>S. Prussin, *J. Appl. Phys.* **32**, 1876 (1961).

<sup>2</sup>J. C. M. Li, *Metall. Trans. A* **9A**, 1353 (1978).

- <sup>3</sup>S. B. Lee, W. L. Wang, and J. R. Chen, *Mater. Chem. Phys.* **64**, 123 (2000).
- <sup>4</sup>W. L. Wang, S. Lee, and J. R. Chen, *J. Appl. Phys.* **91**, 9584 (2002).
- <sup>5</sup>S.-C. Ko, S. Lee, and Y. T. Chou, *Mater. Sci. Eng., A* **409**, 145 (2005).
- <sup>6</sup>F. Q. Yang and J. C. M. Li, *J. Appl. Phys.* **93**, 9304 (2003).
- <sup>7</sup>F. Q. Yang, *Mater. Sci. Eng., A* **409**, 153 (2005).
- <sup>8</sup>J. Christensen and J. Newman, *J. Electrochem. Soc.* **153**, A1019 (2006).
- <sup>9</sup>X. Zhang, W. Shyy, and A. M. Sastry, *J. Electrochem. Soc.* **154**, A910 (2007).
- <sup>10</sup>J. O. Besenhard, J. Yang, and M. Winter, *J. Power Sources* **68**, 87 (1997).
- <sup>11</sup>J. Wolfenstine, *J. Power Sources* **79**, 111 (1999).
- <sup>12</sup>R. A. Huggins and W. D. Nix, *Ionics* **6**, 57 (2000).
- <sup>13</sup>"Basic Research Needs for Electrical Energy Storage—Report of the Basic Energy Sciences Workshop for Electrical Energy Storage," Office of Basic Energy Sciences, Department of Energy report, 2007 (available at [http://www.sc.doe.gov/bes/reports/files/EES\\_rpt.pdf](http://www.sc.doe.gov/bes/reports/files/EES_rpt.pdf)).
- <sup>14</sup>J.-M. Tarascon and M. Armand, *Nature (London)* **414**, 359 (2001).
- <sup>15</sup>A. S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon, and W. Van Schalkwijk, *Nature Mater.* **4**, 366 (2005).
- <sup>16</sup>R. B. Lewis, A. Timmons, R. E. Mar, and J. R. Dahn, *J. Electrochem. Soc.* **154**, A213 (2007).
- <sup>17</sup>K. C. Chan, H. Peng, C. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, and Y. Cui, *Nat. Nanotechnol.* **3**, 31 (2008).
- <sup>18</sup>J. Graetz, C. C. Ahn, R. Yazami, and B. Fultz, *Electrochem. Solid-State Lett.* **6**, A194 (2003).
- <sup>19</sup>P. Patel, I. S. Kim, and P. N. Kumta, *Mater. Sci. Eng., B* **116**, 374 (2005).
- <sup>20</sup>Y. Li and Y.-T. Cheng, *J. Alloys Compd.* **223**, 6 (1995).
- <sup>21</sup>J. W. Gibbs, *The Scientific Papers of J. Willard Gibbs* (Longmans-Green, London, 1906), Vol. 1, p. 55.
- <sup>22</sup>R. C. Cammarata, *Prog. Surf. Sci.* **46**, 1 (1994).
- <sup>23</sup>P. Müller and A. Saúl, *Surf. Sci. Rep.* **54**, 157 (2004).
- <sup>24</sup>A. I. Rusanov, *Surf. Sci. Rep.* **58**, 111 (2005).
- <sup>25</sup>F. D. Fischer, T. Waitz, D. Vollath, and N. K. Simha, *Prog. Mater. Sci.* **53**, 481 (2008).
- <sup>26</sup>R. Shuttleworth, *Proc. Phys. Soc., London, Sect. A* **63**, 444 (1950).
- <sup>27</sup>M. E. Gurtin and A. Murdoch, *Arch. Ration. Mech. Anal.* **57**, 291 (1975).
- <sup>28</sup>M. E. Gurtin and A. Murdoch, *Int. J. Solids Struct.* **14**, 431 (1978).
- <sup>29</sup>M. E. Gurtin, J. Weissmuller, and F. Larche, *Philos. Mag. A* **78**, 1093 (1998).
- <sup>30</sup>P. Sharma, S. Ganti, and N. Bhate, *Appl. Phys. Lett.* **82**, 535 (2003); **89**, 049901 (2006).
- <sup>31</sup>R. E. Miller and V. B. Shenoy, *Nanotechnology* **11**, 139 (2000).
- <sup>32</sup>S. P. Timoshenko and J. N. Goodier, *Theory of Elasticity*, 3rd ed. (McGraw-Hill, New York, 1970).
- <sup>33</sup>L. Vitos, A. V. Ruban, H. L. Skriver, and J. Kollár, *Surf. Sci.* **411**, 186 (1998).
- <sup>34</sup>H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed. (Clarendon, Oxford, 1959).