

## Diffusion-induced stress in inhomogeneous materials: concentration-dependent elastic modulus

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By incorporating the contribution of solute atoms to the Helmholtz free energy of solid solution, a linear relation is derived between Young's modulus and the concentration of solute atoms. The solute atoms can either increase or decrease Young's modulus of solid solution, depending on the first-order derivative of the Helmholtz free energy with respect to the concentration of solute atoms. Using this relation, a closed-form solution of the chemical stress in an elastic plate is obtained when the diffusion behavior in the plate can be described by the classical Fick's second law with convection boundary condition on one surface and zero flux on the other surface. The plate experiences tensile stress after short diffusion time due to asymmetrical diffusion, which will likely cause surface microcracking. The results show that the effect of the concentration dependence of Young's modulus on the evolution of chemical stress in elastic plates is negligible if the change of Young's modulus due to the diffusive motion of solute atoms is not compatible in magnitude with Young's modulus of the pure material. Also, a new diffusion equation is developed for strictly regular binary solid solution. The effective diffusivity is a nonlinear function of the concentration of solute atoms.

**diffusion-induced stresses, concentration-dependent elastic modulus**

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### List of main symbols

$c$	concentration of solute atoms
$i_{\text{reaction}}$	anodic or cathodic current density at the surface of the plate
$n$	number of participating electrons
$u_i (i=1, 2, 3)$	components of the displacement vector
$C_{ijkl}$	stiffness tensor
$D_0$	diffusivity of solute atoms
$D_{\text{eff}}$	effective diffusivity of solute atoms
$E$	Young's modulus
$F_j (j=1, 2, 3)$	components of body force
$\mathbf{J}$	vector of the diffusion flux

$M$	mobility of the diffusing component
$R$	gas constant
$S$	entropy
$T$	absolute temperature
$U_l$	internal energy
$U_{\text{strain}}$	strain energy density
$\beta$	charge transfer barrier for the anodic or cathodic reaction
$\nu$	Poisson's ratio
$\mu$	chemical potential
$\gamma$	activity coefficient
$\sigma$	hydrostatic stress
$\sigma_{ij} (i, j=1, 2, 3)$	components of stress tensor
$\varepsilon_{ij} (i, j=1, 2, 3)$	components of strain tensor
$\mathfrak{F}$	Helmholtz free energy

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- $\Omega$  the coefficient of the volume change per mole of solute atoms  
 $\Upsilon$  Faraday's constant

The migration of solute atoms or molecules in solid materials can cause distortion of local structure [1] and local solid reaction including formation of intermetallic compounds [2–5], which creates local mechanical stress, referred to as diffusion-induced stress or chemical stress [6,7]. The effect of chemical stress on structural evolution and structural degradation can be observed in a variety of material systems and in electronic interconnects. For example, the fast diffusion of Cu in Sn can lead to the formation of intermetallic compound of  $\text{Cu}_6\text{Sn}_5$  in the grain boundaries of Sn-Cu alloy, which can create local stress and cause spontaneous formation of Sn-whiskers. During electrochemical cycling, the insertion and de-insertion of Li-atoms into the active materials in Li-ion batteries, such as graphite and silicon, can cause volumetric change and lead to microcracking of negative electrode [8]. The chemical stress due to the doping of impurities in semiconductor materials can initiate generation of dislocations which affect distribution of solute atoms and electronic behavior of semiconductors [9] due to the interaction between dislocations and solute atoms.

Prussin [6] was the first to analyze the phenomenon of diffusion-induced stress. Li [7] analyzed the evolution of diffusion-induced stress in elastic materials of simple geometries. Lee and co-workers [10–12] studied the evolution of chemical stresses in composite materials. Yang and Li [13] analyzed the bending of an elastic beam induced by the diffusion of solute atoms. Chu and Lee [14] used Li's solution [7] to analyze the effect of chemical stresses on diffusion without addressing the coupling effect. Zhang et al. [15] considered the effects of absorption and desorption and used the convection boundary condition in analyzing the evolution of chemical stress in a membrane. They revealed that the boundary conditions play an important role in the stress evolution. Kandasamy [16] considered the influence of self-induced stress on the temporal-spatial variation of concentration during the diffusion of hydrogen in a palladium and proposed a quadratic steady-state concentration profile. Considering the interaction between diffusion and chemical stress, Yang [17] derived a diffusion equation taking account of the effect of stress-induced diffusion and established a relationship between hydrostatic stress and concentration of solute atoms and obtained a general relation among the surface concentration of solute atoms, normal stress and surface deformation of a solid. Later, Zhang et al. [18] considered the effect of stress-induced diffusion and analyzed the intercalation-induced stress in Li-ion battery electrode particles. Kalnaus et al. [19] recently used the theory of diffusion-induced stress and a fracture damage parameter to analyze the fracture of silicon particles due to Li-ion intercalation. Most of these analyses have considered the diffusion-induced stress in homogeneous materials

without considering the concentration-dependent elastic properties of materials.

It is known that the presence of impurities in a solid can alter local structure and cause the change in local mechanical response. Soma et al. [20] used the microscopic electronic theory to calculate the concentration dependence of the elastic moduli of Al-Si and Al-Ge solid solutions from the first principles. Their results showed that the elastic constants decrease with increasing the concentration of solute atoms (Si and Ge). In contrast to the results for the systems of Al-Si and Al-Ge solid solutions, Soma et al. [21] also found that the elastic modulus of Al-Cu solid solution increases with increasing the concentration of Cu solute atoms. Recently, Qi et al. [22,23] used density functional theory to calculate the dependence of the elastic modulus of lithiated graphite, Li-Si amorphous and crystalline structures on lithium concentration and demonstrated the effect of Li-concentration on the elastic properties of the active materials used in Li-ion batteries. Using the results from Qi et al. [22,23], Deshpande et al. [24] numerically analyzed the effect of concentration-dependent elastic modulus on the diffusion-induced stress in an elastic cylinder.

Considering the important role of diffusion-induced stress in controlling the structural and electrochemical integrity of Li-ion batteries, I present a thermodynamic model to describe the concentration-dependence of elastic properties of solid solutions. A general relationship between the Young's modulus of a solid solution and the concentration of solute atoms is derived. The effect of the atomic/molecular interaction in non-ideal solid solutions on the diffusion equation is also discussed.

## 1 Concentration dependence of elastic constants

Consider an elastic solid made of solid solution and subjected to mechanical loading. The deformation and stress states of the solid are determined by a stress tensor,  $\sigma_{ij}$  ( $i, j=1, 2, 3$ ), and a strain tensor,  $\varepsilon_{ij}$ . The increment of strain energy per unit volume,  $U_{\text{strain}}$ , can be calculated by

$$dU_{\text{strain}} = \sum_{i,j=1}^3 \sigma_{ij} d\varepsilon_{ij}, \quad (1)$$

from which the mechanical work per unit volume done to the solid is

$$dW = -dU_{\text{strain}} = -\sum_{i,j=1}^3 \sigma_{ij} d\varepsilon_{ij}. \quad (2)$$

Assume that the deformation occurs slowly and thermodynamic equilibrium is established in the solid at every instant. The first and second laws of thermodynamics give

$$dU_I = TdS - dW = TdS + \sum_{i,j=1}^3 \sigma_{ij} d\varepsilon_{ij}, \quad (3)$$

where  $U_I$  is internal energy,  $T$  is absolute temperature, and  $S$  is entropy. From definition of the Helmholtz free energy,  $\mathfrak{F} = U_I - TS$ , there is

$$d\mathfrak{F} = -SdT + \sum_{i,j=1}^3 \sigma_{ij} d\varepsilon_{ij}, \quad (4)$$

which gives

$$\sigma_{ij} = \left. \frac{\partial \mathfrak{F}}{\partial \varepsilon_{ij}} \right|_{T, \varepsilon'_{ij}}. \quad (5)$$

Using eq. (5), the stiffness tensor,  $C_{ijkl}$ , can be calculated as:

$$C_{ijkl} = \left. \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \right|_{\varepsilon'_{ij}} = \left. \frac{\partial^2 \mathfrak{F}}{\partial \varepsilon_{kl} \partial \varepsilon_{ij}} \right|_{T, \varepsilon'_{ij}}. \quad (6)$$

The subscript  $\varepsilon'_{ij}$  means that all other  $\varepsilon_{ij}$  remain constant when taking the derivative with respect to  $\varepsilon_{ij}$ . For an elastic solid made of solid solution, one can expand the Helmholtz free energy of  $\mathfrak{F}$  in a Taylor series as:

$$\mathfrak{F}(\varepsilon_{ij}, c) = \mathfrak{F}(\varepsilon_{ij}, 0) + \frac{\partial \mathfrak{F}(\varepsilon_{ij}, 0)}{\partial c} c + \frac{1}{2} \frac{\partial^2 \mathfrak{F}(\varepsilon_{ij}, 0)}{\partial c^2} c^2 + \dots, \quad (7)$$

where  $c$  is the concentration of solute atoms. Substitution of eq. (7) in eq. (6) yields

$$C_{ijkl} = C_{ijkl}^0 + \left. \frac{\partial^3 \mathfrak{F}(\varepsilon_{ij}, 0)}{\partial \varepsilon_{kl} \partial \varepsilon_{ij} \partial c} \right|_{T, \varepsilon'_{ij}} c + \dots \equiv C_{ijkl}^0 + (\Delta C_{ijkl})c + \dots \quad (8)$$

with  $C_{ijkl}^0$  being the elastic constants without the presence of solute atoms and  $\Delta C_{ijkl}$  being the change of the elastic constants per unit concentration of solute atoms. To a first order of approximation, the elastic constants are a linear function of the concentration of solute atoms. Depending on the contribution of solute atoms to the solid solution, the elastic constants can either increase or decrease with increasing the concentration of solute atoms. For isotropic materials, eq. (8) gives the concentration dependence of Young's modulus to the first order of the solute concentration as:

$$E = E_0 + \chi c \quad (9)$$

with  $E_0$  being Young's modulus without the presence of solute atoms and  $\chi$  being the change of Young's modulus per unit concentration of solute atoms.

It is worth pointing out that the linear dependence of elastic constants on the concentration of second phase is well-known for particulate composites of diluent concentration [25–28]. The intrinsic elastic constants can also either increase or decrease with increasing the concentration of second phase, depending on the ratio of the elastic constants

of matrix to those of particulate.

## 2 Mathematical formula of the coupling problem

### 2.1 Governing equation of mechanical equilibrium

Assume that the local deformation induced by solute atoms is small and the material is isotropic. Thus the theory of linear elasticity can be applied to analyze the deformation induced by diffusion and migration of solute atoms as used by Prussin [6] and Li [7]. The relationships between the components of the strain tensor ( $\varepsilon_{ij}$ ) and the components of the displacement vector ( $u_i, i=1, 2, 3$ ) are

$$\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (10)$$

and the constitutive relations describing the diffusion-induced deformation are

$$\varepsilon_{ij} = \frac{1}{E} [(1 + \nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij}] + \frac{C\Omega}{3}. \quad (11)$$

Here,  $\Omega$  is the coefficient of the volume change per mole of solute atoms, and  $\nu$  is Poisson's ratio of the material. The Young's modulus  $E$  is a function of the concentration of solute atoms as given in eq. (9) and the Poisson's ratio is assumed to be a constant independent of  $c$ .

In general, the characteristic time for elastic deformation of solids is much smaller than that for atomic diffusion and migration. Thus, the elastic deformation induced by the diffusion of solute atoms can be reasonably approximated as quasi-static process, and mechanical equilibrium is attained instantaneously. The equilibrium equations describing the elastic deformation of a solid are

$$\sum_{i=1}^3 \frac{\partial \sigma_{ij}}{\partial x_i} + F_j = 0, \quad (j=1, 2, 3), \quad (12)$$

where  $F_j$  ( $j=1, 2, 3$ ) denote the components of body force along the corresponding direction. From eq. (10) to eq. (12), one can note that the diffusion-induced stress is analogous to thermal stress created by gradient of temperature in an otherwise stress-free solid.

Using eq. (9), the constitutive equations of (11) and the relation between the components of the strain tensor and the components of the displacement vector of (10) in eq. (12), one has

$$\begin{aligned} G\nabla^2 u_j + \frac{G}{1-2\nu} \sum_{i=1}^3 \frac{\partial^2 u_i}{\partial x_j \partial x_i} + \frac{2\nu}{1-2\nu} \frac{\partial G}{\partial x_j} \sum_{i=1}^3 \frac{\partial u_i}{\partial x_i} \\ + \sum_{i=1}^3 \frac{\partial G}{\partial x_i} \left( \frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j} \right) - \frac{\Omega c}{3(1-2\nu)} \frac{\partial E}{\partial x_j} = K\Omega \frac{\partial c}{\partial x_j} - F_j, \end{aligned} \quad (j=1, 2, 3), \quad (13)$$

where  $G$  and  $K$  are the shear and bulk moduli of the solid, respectively, related to Young's modulus as:

$$G = \frac{E}{2(1+\nu)}, \quad K = \frac{E}{3(1-2\nu)}. \quad (14)$$

Eq. (13) governs the diffusion-induced stress in inhomogeneous, elastic materials. Substituting eq. (9) into eq. (13) gives

$$\begin{aligned} & \frac{E_0 + \chi c}{2(1+\nu)} \nabla^2 u_j + \frac{E_0 + \chi c}{2(1+\nu)(1-2\nu)} \sum_{i=1}^3 \frac{\partial^2 u_i}{\partial x_j \partial x_i} \\ & + \frac{\nu \chi}{(1+\nu)(1-2\nu)} \frac{\partial c}{\partial x_j} \sum_{i=1}^3 \frac{\partial u_i}{\partial x_i} \\ & + \frac{\chi}{2(1+\nu)} \sum_{i=1}^3 \frac{\partial c}{\partial x_i} \left( \frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j} \right) - \frac{\chi \Omega c}{3(1-2\nu)} \frac{\partial c}{\partial x_j} \\ & = \frac{E_0 + \chi c}{2(1+\nu)} \Omega \frac{\partial c}{\partial x_j} - F_j. \end{aligned} \quad (15)$$

Both the concentration and concentration gradient of solute atoms contribute to the evolution of local deformation in materials. For homogeneous materials with Young's modulus independent of the concentration of solute atoms, there is  $\chi=0$  and eq. (15) is reduced to the result given by Yang [17].

To completely describe the problem, one needs the boundary conditions to obtain the deformation and stress fields from eq. (15) and the diffusion field. Depending on the loading and displacement conditions, both the stress and displacement can be pre-described on portions of the boundary similar to the theory of linear elasticity.

## 2.2 Diffusion equation

Based on thermodynamics, the chemical potential ( $\mu$ ) in a solid solution can be written as:

$$\mu = \mu_0 + RT \ln \gamma c - \alpha \Omega, \quad (16)$$

where  $\mu_0$  is a constant,  $R$  is the gas constant,  $\gamma$  is the activity coefficient, and  $\sigma$  is hydrostatic stress. Using eq. (16), the diffusion flux being proportional to the gradient of chemical potential can be expressed as:

$$\mathbf{J} = -Mc \nabla \mu = -D_0 \left( \nabla c + c \nabla \ln \gamma - \frac{\Omega c}{RT} \nabla \sigma \right), \quad (17)$$

where  $\mathbf{J}$  is the vector of the diffusion flux,  $M$  is the mobility of the diffusing component, and  $D_0$  is the diffusivity of solute atoms in a stress-free solid. Eq. (17) is reduced to the result for an ideal solid solution, i.e.,  $\gamma=1$  [17]. In contrast to ideal solid solutions, the diffusion flux is dependent on the interaction between solvent atoms and solute atoms for regular solid solution.

For a strictly regular binary solution, there is [29]

$$\ln \gamma = \alpha(1-c)^2. \quad (18)$$

The factor  $\alpha$  represents the difference in interaction between similar atoms and two dissimilar atoms in the solution. Substitution of eq. (18) in eq. (17) gives

$$\mathbf{J} = -Mc \nabla \mu = -D_0 \left( [1-2\alpha(1-c)c] \nabla c - \frac{\Omega c}{RT} \nabla \sigma \right). \quad (19)$$

If the hydrostatic stress is only a function of the concentration of solute atoms, one can define the effective diffusivity of solute atoms ( $\mathbf{D}_{\text{eff}}$ ) in a stressed solid as:

$$\begin{aligned} \mathbf{D}_{\text{eff}} &= MRT \left[ 1 - 2\alpha(1-c)c - \frac{\Omega c}{RT} \frac{\partial \sigma}{\partial c} \right] \\ &= D_0 \left[ 1 - 2\alpha(1-c)c - \frac{\Omega c}{RT} \frac{\partial \sigma}{\partial c} \right]. \end{aligned} \quad (20)$$

The interaction between two dissimilar atoms introduces quadratic dependence of the effective diffusivity on the concentration of solute atoms even when the solid is at a stress-free state. Using the law of mass conservation:

$$\nabla \cdot \mathbf{J} = -\frac{\partial c}{\partial t}, \quad (21)$$

the diffusion equation accounting for the effect of stress-induced diffusion can be written as

$$\begin{aligned} & D_0 \left( [1-2\alpha(1-c)c] \nabla^2 c - 2\alpha(1-2c) \nabla c \cdot \nabla c \right. \\ & \left. - \frac{\Omega}{RT} \nabla c \cdot \nabla \sigma - \frac{\Omega c}{RT} \nabla^2 \sigma \right) = \frac{\partial c}{\partial t}. \end{aligned} \quad (22)$$

For the hydrostatic stress being proportional to the concentration with the proportionality of the ratio  $\xi$ , independent of spatial variables, eq. (22) can be written as

$$\begin{aligned} & D_0 \left( \left[ 1 - 2\alpha(1-c)c - \frac{\xi \Omega c}{RT} \right] \nabla^2 c - \left[ 2\alpha(1-2c) + \frac{\xi \Omega}{RT} \right] \nabla c \cdot \nabla c \right) \\ & = \frac{\partial c}{\partial t}. \end{aligned} \quad (23)$$

Finally, one needs to have the boundary conditions, such as the concentration condition or the flux condition on portions of the boundary in order to numerically or analytically solve the diffusion equation (23) for a given stress field.

## 3 Evolution of chemical stress in an elastic thin plate

In general, it is very difficult to obtain analytical solutions of chemical stress in elastic solids due to the coupling between diffusion and stress as given in eqs. (15) and (23). To obtain a closed-form solution of chemical stress, we assume

that the effect of stress on the diffusion of solute atoms is negligible and the solid solution is an ideal solution in the following analysis of the stress evolution in an elastic thin plate. Thus the diffusion of solute atoms in the plate can be described by the classical Fick's second law.

### 3.1 Concentration field

Consider a conducting, elastic thin plate in the region  $0 \leq x \leq L$ ,  $-\infty < y < \infty$ , and  $-\infty < z < \infty$ . The elastic plate functions as an electrode in an electrochemical environment; and solute atoms diffuse into the plate similar to the diffusion of lithium in electric anode in a Li-ion battery. To obtain a closed-form solution, assume that the effect of stress on the diffusion of solute atoms in the plate is negligible. Thus, the diffusion of solute atoms in the plate satisfies Fick's second law as:

$$\frac{\partial c}{\partial t} = D_0 \frac{\partial^2 c}{\partial x^2}. \tag{24}$$

Initially, there are no solute atoms in the plate, i.e., the initial condition is

$$c = 0, \text{ for } 0 \leq x \leq L \text{ at } t=0. \tag{25}$$

The conducting plate is connected to the current collector at the end of  $x=0$  and solute atoms cannot diffuse into the plate. Thus, the boundary condition at  $x=0$  is

$$\frac{\partial c}{\partial x} = 0, \text{ for } t \geq 0 \text{ at } x=0. \tag{26}$$

The polarization of an electrode supporting the electrochemical reaction at the electrolyte-electrode interface is given in the Butler-Volmer equation [30,31] as:

$$i_{\text{reaction}} = i_0 [e^{(1-\beta)nY\eta/RT} - e^{-\beta nY\eta/RT}], \tag{27}$$

where  $i_{\text{reaction}}$  is the anodic or cathodic current density at the surface of the plate,  $i_0$  is the exchange current density,  $\beta$  is charge transfer barrier (symmetry coefficient) for the anodic or cathodic reaction,  $n$  is the number of participating electrons, and  $Y$  is Faraday's constant. The surface overpotential of  $\eta$  is equal to  $V-U$ , where  $V$  is the applied surface potential of the plate and  $U$  is the equilibrium potential. For  $nY\eta/RT \ll 1$ , eq. (27) can be approximated to the first order of  $nY\eta/RT$  as:

$$i_{\text{reaction}} = \frac{i_0 n Y \eta}{RT} = \frac{i_0 n Y}{RT} (V - U). \tag{28}$$

For  $t \rightarrow \infty$ , the electrochemical system approaches an equilibrium state with the overpotential tending to zero and  $U \rightarrow U_s = V$ . Using the Taylor series expansion about the equilibrium state to the first order of  $(c - c_s)$ , one has

$$i_0 \approx i_0|_s + \frac{\partial i_0}{\partial c} (c - c_s), \tag{29}$$

$$U \approx U_s + \frac{\partial U}{\partial c} (c - c_s) = V + \frac{\partial U}{\partial c} (c - c_s). \tag{30}$$

Substituting eqs. (29) and (30) into eq. (28) yields

$$i_{\text{reaction}} = -\frac{i_0|_s n Y}{RT} \frac{\partial U}{\partial c} (c - c_s) \tag{31}$$

to the first order of  $(c - c_s)$ . Here, the subscript  $s$  represents the equilibrium state with the current and overpotential approaching zero, i.e.,  $i_{\text{reaction}} \rightarrow 0$ , at which the solute atoms uniformly distribute in the plate. Thus, the diffusion flux of solute atoms at the electrolyte-electrode interface of the plate is

$$j = \frac{i_{\text{reaction}}}{Y} = -D_0 \frac{\partial c}{\partial x} \Big|_{\text{surface}} \approx -\frac{i_0|_s n}{RT} \frac{\partial U}{\partial c} (c - c_s), \tag{32}$$

which gives the boundary condition as:

$$\frac{\partial c}{\partial x} = -\frac{\kappa}{L} (c - c_s), \text{ at } x=L \tag{33}$$

with

$$\kappa = -\frac{i_0|_s n L}{D_0 RT} \frac{\partial U}{\partial c} \Big|_s. \tag{34}$$

Using the separation of variables, one can obtain the temporal-spatial distribution of the solute atoms in the plate as:

$$\frac{c}{c_s} = 1 - 2\kappa \sum_{n=1}^{\infty} \frac{1}{\beta_n^2 + \kappa^2 + \kappa} \frac{\cos(\beta_n x / L)}{\cos \beta_n} e^{-D_0 \beta_n^2 t / L^2}, \tag{35}$$

where  $\beta_n$ 's are the positive roots of

$$\beta_n \tan \beta_n = \kappa. \tag{36}$$

### 3.2 Chemical stress field

Following the approach used in the analysis of thermoelastic stress in an elastic thin plate with stress-free condition as  $|y| \rightarrow \infty$  and  $|z| \rightarrow \infty$  [32], one can express the chemical stress in the plate as:

$$\sigma_{yy} = \sigma_{zz} = \frac{\Omega E}{3(1-\nu)} (-c + \aleph + \upsilon x). \tag{37}$$

The parameters of  $\aleph$  and  $\upsilon$  are two constants to be determined. The condition of the plate being free from external loading requires

$$\int_0^L \sigma_{yy} dx = \int_0^L \sigma_{zz} dx = 0, \tag{38}$$

$$\int_0^L \sigma_{yy} x dx = \int_0^L \sigma_{zz} x dx = 0. \tag{39}$$

Assume that both  $\Omega$  and  $\nu$  are constants. Substitution of eq. (37) into eqs. (38) and (39) yields

$$\mathfrak{N} = \frac{\int_0^L Ecdx \int_0^L Ex^2 dx - \int_0^L Exdx \int_0^L Ecx^2 dx}{\int_0^L Edx \int_0^L Ex^2 dx - \left(\int_0^L Exdx\right)^2}, \quad (40)$$

$$\nu = \frac{\int_0^L Edx \int_0^L Ecxdx - \int_0^L Exdx \int_0^L Ecdx}{\int_0^L Edx \int_0^L Ex^2 dx - \left(\int_0^L Exdx\right)^2}, \quad (41)$$

which is reduced to the result for constant elastic modulus. For Young's modulus being a linear function of the concentration of solute atoms as given in eq. (9), there are

$$\int_0^L Edx = E_0L + \chi \int_0^L cdx, \quad (42)$$

$$\int_0^L Exdx = \frac{E_0L^2}{2} + \chi \int_0^L cxdx, \quad (43)$$

$$\int_0^L Ex^2 dx = \frac{E_0L^3}{3} + \chi \int_0^L cx^2 dx, \quad (44)$$

$$\int_0^L Ecdx = E_0 \int_0^L cdx + \chi \int_0^L c^2 dx, \quad (45)$$

$$\int_0^L Ecxdx = E_0 \int_0^L cxdx + \chi \int_0^L c^2 x dx, \quad (46)$$

$$\int_0^L Ecx^2 dx = E_0 \int_0^L cx^2 dx + \chi \int_0^L c^2 x^2 dx. \quad (47)$$

Obviously, the chemical stress in the plate is dependent on the distribution of solute atoms as well as the solute concentration of  $c_s$ . Using eq. (35), one can determine the temporal-spatial evolution of the chemical stress as induced by the diffusion of solute atoms.

Consider the stress evolution as introduced by the insertion of Li-atoms into a graphite plate of 1  $\mu\text{m}$  in thickness in a Li-ion battery during a charging process. The parameter of  $\chi$  is approximately equal to  $3E_0$ , as given by Deshpande et al. [24]. The other parameters used in the calculation are  $c_s=0.05$  and  $\kappa=0.05$ . The use of  $c_s=0.05$  means that the solid solution can be treated as an ideal solution and the effect of stress-assisted diffusion is negligible, which is in accord with the use of Fick's second law in analyzing the distribution of solute atoms in the plate as given in eq. (35).

Figure 1 shows the distribution of the chemical stress in the graphite plate at various times. Most portion of the plate experience tensile stress. The position of the maximum tensile stress changes with time, which shifts from the near-surface position ( $x=L$ ) to the center of the plate. It is interesting to note that both surfaces also experiences tensile stress after short diffusion time in contrast to the evolution of the chemical stress in an elastic plate induced by

symmetrically diffusive motion of solute atoms into both surfaces. Such a tensile stress state is due to the asymmetrical feature of the diffusive motion of the solute atoms and reveals the possibility of creating surface microcracks during the insertion of Li-atoms into active materials, since microcracking had been observed in Si-based electric anode during the electrochemical cycling of thin film Li-ion battery [8].

The temporal evolution of the chemical stress in the graphite plate at two positions ( $x=L$  and  $x=L/2$ ) is depicted in Figure 2. The center of the plate always experiences tensile stress, while the surface of plate with the convection boundary condition of (33) first experiences compressive stress and then tensile stress with the increase of time. The change from the compressive stress state to the tensile stress state in the plate near the surface represents the effect of diffusion boundary conditions on the stress evolution in the plate. For asymmetrical diffusion motion of solute atoms, the non-zero parameter of  $\nu$  as given in eq. (41) alters local stress state and leads to the transition of the chemical stress

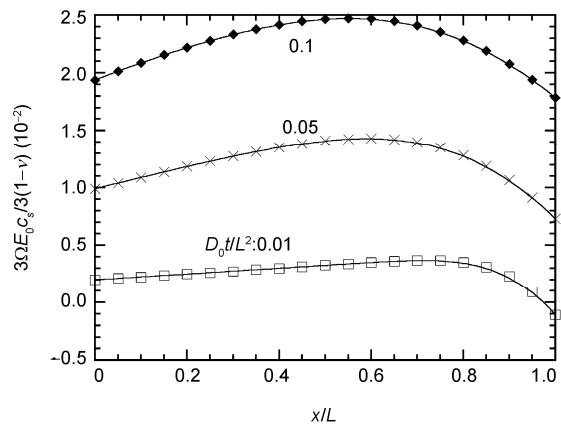


Figure 1 Spatial distribution of the chemical stress in the elastic plate at various times ( $\chi=3E_0$ ,  $L=1 \mu\text{m}$ ,  $c_s=0.05$  and  $\kappa=0.05$ ).

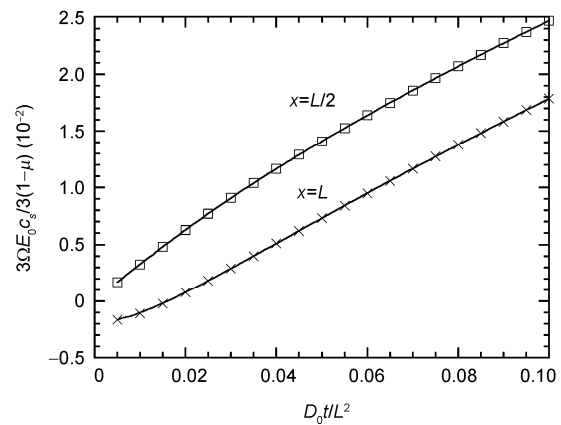


Figure 2 Time dependence of the chemical stress in the elastic plate at two positions of  $x=L/2$  and  $x=L$  ( $\chi=3E_0$ ,  $L=1 \mu\text{m}$ ,  $c_s=0.05$  and  $\kappa=0.05$ ).

near the surface with the convection boundary condition from compressive stress state to tensile stress state.

To examine if the concentration dependence of Young's modulus plays a key role in the evolution of the chemical stress, we calculate the stress evolution in the graphite plate for  $\chi=0$  and  $-3E_0$ . No significant difference in the temporal-spatial evolution of the chemical stress among these three cases is observed, which suggests that, for  $\chi=3E_0$  the evolution of chemical stress in the graphite plate is primarily controlled by the diffusion of the solute atoms as determined by the boundary conditions. From eq. (9), one has

$$E = E_0(1 + \chi c / E_0). \quad (48)$$

To observe the effect of the concentration-dependence of Young's modulus on the chemical stress, it generally requires that  $\chi c / E_0 \sim O(1)$ , i.e.,

$$\chi \sim \frac{E_0}{\int_0^L c dx / L} \equiv \frac{E_0}{\langle c \rangle}. \quad (49)$$

For dilute solid solution with  $\langle c \rangle$  being 0.05, it needs  $\chi \sim 20E_0$  in order to have observable effect. In other words, the concentration-dependence of Young's modulus generally has negligible effect on the evolution of chemical stress in solid solutions. However, such an effect may become important when new phases are formed during the diffusive motion of solute atoms and the material becomes composite.

## 4 Summary

Understanding the diffusion-induced stress in solid materials plays an important role in determining the structural durability in chemical and electrochemical environments. Taking account of the contribution of solute atoms to the Helmholtz free energy of solute solution, the dependence of Young's modulus on the concentration of solute atoms is derived to the first order of the concentration of solute atoms. The solute atoms can either increase or decrease the Young's modulus of solid solution, depending on the first-order derivative of the Helmholtz free energy with respect to the concentration of solute atoms. The dependence of Young's modulus on the concentration of solute atoms is then included in deriving the mechanical equilibrium equation. The result shows that both the concentration and concentration gradient of solute atoms contribute to the evolution of local deformation in materials.

The effect of the concentration dependence of Young's modulus on the evolution of chemical stress in an elastic plate is discussed. A closed-form solution of the chemical stress is obtained. Assuming that the diffusion behavior in the plate can be described by the classical Fick's second law

with convection boundary condition on one surface and zero flux on the other surface to mimic the electrochemical charging of a thin-film-based electric anode in a Li-ion battery, we have analyzed the temporal-spatial distribution of the chemical stress. The results show that the plate experiences tensile stress after short diffusion time due to the asymmetrical diffusion, which will likely cause local structural degradation and lead to pre-mature failure of the plate during the charging process. In addition, it turns out that the effect of the concentration dependence of Young's modulus on the evolution of chemical stress in elastic plates is negligible if the magnitude of  $\chi c$  is not compatible with  $E_0$ .

Considering the interaction between solute atoms and solvent atoms, a new diffusion equation is developed for strictly regular binary solid solution. The effective diffusivity is a nonlinear function of the concentration of solute atoms. Such a relation reveals the importance of the atomic/molecular interaction in controlling the diffusive motion of atoms and molecules.

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