

Interaction between diffusion and chemical stresses

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Abstract

The present work studies the interaction between chemical stresses and diffusion. A new relation between hydrostatic stress and concentration of solute atoms is established. For a solid free of action of body force, the Laplacian of the hydrostatic stress is proportional to the Laplacian of the concentration of solute atoms, that is, deviation of the hydrostatic stress from its local average is proportional to deviation of the local concentration of solute atoms. A general relationship among surface concentration of solute atoms, normal stress and surface deformation of a solid is then derived, in which the normal stress is dependent on the mean curvature of the undeformed surface and tangential components of the surface displacement. A closed-form solution of the steady state concentration of solute atoms in a thin plate is obtained. It turns out that linear distribution of solute atoms in the plate is non-existent due to the interaction between chemical stresses and diffusion.

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1. Introduction

It is known that diffusion of atoms in materials could lead to the evolution of local stresses, which has been referred as diffusion-induced stresses or chemical stresses [1,2]. The effect of chemical stresses on material behavior can be observed in different material systems and be used in a variety of microelectronic and micromechanical systems. For examples, the use of Cu and low-K dielectrics in high-performance CMOS devices imposes a challenge in the control of the diffusion of Cu as degradation of time-dependent dielectric breakdown (TDDB) in Cu metallization is related to the diffusion of Cu ion caused by electrical stress and the TDDB lifetime depends on the breakdown voltage of the low-K material. Impurities have been doped in semiconductor materials to alter the Fermi level for the design of microelectronic devices [3], while the diffusion-induced stresses could initiate generation of dislocations and affect distribution of impurities and related electronic behavior. Diffusion of hydrogen into metals can introduce hydrogen-induced cracking and hydrogen-enhanced local plasticity [4]. The evolution of stresses during diffusion was originally analyzed by Prussin [1]. Li [2] studied the diffusion-induced stresses in elastic media of simple geometries. Lee and co-workers [5,6] analyzed the effect in

composite materials. Larch and Cahn [7,8] investigated the stresses arising from inhomogeneities in materials. Recently, Yang and Li [9] considered the effect of chemical stresses on the bending of beam/plate structure.

The effects of stresses on creep deformation involving diffusion of vacancies were proposed by Nabarro [10] and Herring [11]. Li addressed the effect of stresses on the effective diffusivity for a given stress field [2] and Chu and Li [12] analyzed the stress-induced diffusion in the impression of a half-space. Yang and Li [13,14] considered the stress-induced diffusion in the impression of thin films. Based on the concept of thermodynamic factor, Alefeld et al. [15] solved the problem of diffusion when subjected to applied stress. Larch and Cahn [7,8] analyzed the effect of stresses on local diffusion in a solid, where the coupling between diffusion and chemical stresses was addressed. The effect of chemical stresses on diffusion was discussed by Chu and Lee [16] using Li's solution [2], while they did not consider the coupling effect. Kandasamy [17] addressed the influence of chemical stresses on space-time variation of concentration during diffusion of hydrogen in a palladium alloy and proposed a quadratic steady-state hydrogen concentration profile. Using Li's solution [2] and neglecting the coupling effect, Zhang et al. [18] reanalyzed the distribution of the steady-state concentration of hydrogen in elastic membranes during hydrogen diffusion. They claimed that nonlinear distribution of concentration is non-existent and linear form is

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the only solution for ideal solid solution. Recently, Aziz analyzed the effects of pressure and stress on diffusion from atomic point view [19] and considered such effects on diffusion in Si [20].

Considering the importance of the coupling between diffusion and chemical stresses in the interpretation of stress relaxation and in the understanding of up-hill diffusion effect in hydrogen permeable metals, we consider the coupling effect on the distribution of concentration of solute atoms in a thin plate. Some new relations between chemical stresses and concentration of solute atoms are formulated, from which an analytical solution of the distribution of the steady-state concentration in a plate is obtained.

2. Mathematical formula of the coupling problem

2.1. Governing equation of mechanical equilibrium

As might be expected, there is a stress field associated with the distorted lattice surrounding a solute atom with size too large or too small in relation to the size of the host atom. Following the approach in analyzing the stress field introduced by dislocations, we only focus on small deformation and assume the material to be an isotropic elastic solid. Thus, the formal theory of linear elasticity can be used for analyzing the stresses and strains created by solute atoms. The relationships between the components (ε_{ij} , $i, j = 1, 2, 3$) of the strain tensor ($\langle \varepsilon \rangle$) and the components (u_i , $i = 1, 2, 3$) of the displacement vector (\vec{u}) are

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

Extending the 1D relation between the strain and the concentration of solute atoms given by Prussin [1] to the 3D case, one can express the constitutive relations as [5]

$$\varepsilon_{ij} = \frac{1}{E} [(1 + \nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij}] + \frac{C\Omega}{3}\delta_{ij} \quad (2)$$

where σ_{ij} are the components of the stress tensor ($\langle \sigma \rangle$); Ω , the partial molar volume of solute (m^3/mol) and C is the concentration (moles/ m^3) of the diffusing component; E and ν are Young's modulus and Poisson's ratio of the material, respectively. The partial molar volume Ω is assumed constant independent of C .

Compared to diffusion of atoms in solids, the characteristic time for elastic deformation of solids is much smaller than that for atomic migration. Thus, mechanical equilibrium is built up in a much faster way than the diffusion process, and the elastic deformation can be treated as quasi-static state, that is, mechanical equilibrium is assumed to be attained instantaneously. It should be pointed out that, in reality a finite amount of time is required for a dynamic wave to propagate across the problem domain, but the wave propagation term is neglected in the quasi-static approximation. The equilibrium equations

describing elastic deformation of a solid are

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

where F_j ($j = 1, 2, 3$) denote the components of body force (\vec{F}) along the corresponding direction. From Eqs. (1)–(3), one can notice that the stresses caused by the diffusion of solute atoms are analogous to those created by gradient of temperature in an otherwise stress-free solid.

Using the constitutive equations of (2) and the relation between the components of the strain tensor and the components of the displacement vector of (1), the equilibrium equations of (3) can be rewritten as

$$G\nabla^2 u_j + \frac{G}{1-2\nu} \sum_{i=1}^3 \frac{\partial^2 u_i}{\partial x_j \partial x_i} = K\Omega \frac{\partial C}{\partial x_j} - F_j \quad (j = 1, 2, 3) \quad (4)$$

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

$$G = \frac{E}{2(1+\nu)} \text{ and } K = \frac{E}{3(1-2\nu)} \quad (5)$$

A concise equation describing the volumetric strain can be obtained from Eq. (4). Expressing the volumetric strain (ϵ) as the divergence of the displacement vector,

$$\epsilon = \frac{\partial u_1}{\partial x_1} + \frac{\partial u_2}{\partial x_2} + \frac{\partial u_3}{\partial x_3} \quad (6)$$

one obtains

$$\nabla^2 \left(\epsilon - \frac{\Omega}{3} \frac{1+\nu}{1-\nu} C \right) = -\frac{1}{3K} \frac{1+\nu}{1-\nu} \vec{\nabla} \cdot \vec{F} \quad (7)$$

Defining the hydrostatic stress as

$$\sigma = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3} \quad (8)$$

and using Eq. (2), the relation between the volumetric strain and the hydrostatic stress can be expressed as

$$\epsilon = \frac{3(1-2\nu)}{E} \sigma + \Omega C \quad (9)$$

Substitution of Eq. (9) into Eq. (7) gives

$$\nabla^2 (\sigma + \alpha C) = -\frac{1+\nu}{3(1-\nu)} \vec{\nabla} \cdot \vec{F} \quad (10)$$

in which

$$\alpha = \frac{2E\Omega}{9(1-\nu)} \quad (11)$$

In the absence of body force, Eq. (10) reduces to

$$\nabla^2 (\sigma + \alpha C) = 0 \quad (12)$$

The Laplacian of the hydrostatic stress is proportional to the Laplacian of the concentration of solute atoms, that is, the deviation of the hydrostatic stress from its local average is proportional to the deviation of the local concentration of solute atoms. If the

effect of concentration is negligible, Eq. (12) becomes the well-known equation in the theory of linear elasticity.

2.2. Diffusion equation

Based on thermodynamics, the chemical potential (μ) in an ideal solid solution can be written as [2],

$$\mu = \mu_0 + RT \ln C - \sigma\Omega \quad (13)$$

where μ_0 is a constant; R , the gas constant; and T , the absolute temperature. Using Eq. (13), the diffusion flux being proportional to the gradient of chemical potential can be expressed as,

$$\vec{J} = -MC\vec{\nabla}\mu = -D_0 \left(\vec{\nabla}C - \frac{\Omega C}{RT} \vec{\nabla}\sigma \right) \quad (14)$$

where \vec{J} is the vector of the diffusion flux and D_0 is the diffusivity of solute atoms in a stress-free solid. If the hydrostatic stress is only a function of the concentration of solute, one can define the effective diffusivity of solute (D_{eff}) in a stressed isotropic solid as

$$D_{\text{eff}} = MRT \left(1 - \frac{\Omega C}{RT} \frac{\partial \sigma}{\partial C} \right) = D_0 \left(1 - \frac{\Omega C}{RT} \frac{\partial \sigma}{\partial C} \right) \quad (15)$$

Using the law of mass conservation,

$$\vec{\nabla} \cdot \vec{J} = -\frac{\partial C}{\partial t} \quad (16)$$

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

$$D_0 \left[\nabla^2 C - \frac{\Omega}{RT} \vec{\nabla}C \cdot \vec{\nabla}\sigma - \frac{\Omega C}{RT} \nabla^2 \sigma \right] = \frac{\partial C}{\partial t} \quad (17)$$

If the hydrostatic stress is proportional to the concentration with the proportionality of the ratio ξ , independent of spatial variables, Eq. (17) reduces to

$$\left(1 - \frac{\Omega C}{RT} \xi \right) \nabla^2 C - \frac{\Omega}{RT} \xi (\vec{\nabla}C \cdot \vec{\nabla}C) = \frac{1}{D_0} \frac{\partial C}{\partial t} \quad (18)$$

2.3. Correlation between normal stress and surface displacement

Let \vec{n} and \vec{t} be the unit normal and tangent vectors of an undeformed surface, $\tilde{\Omega}$. The gradient operator $\vec{\nabla}$ on the surface $\tilde{\Omega}$ can be expressed as

$$\vec{\nabla} = (\langle I \rangle - \vec{n}\vec{n}) \cdot \vec{\nabla} + \vec{n}\vec{n} \cdot \vec{\nabla} = \vec{\nabla}_S + \vec{n}\vec{n} \cdot \vec{\nabla} \quad (19)$$

where $\langle I \rangle$ is the unit tensor and $\vec{\nabla}_S = (\langle I \rangle - \vec{n}\vec{n}) \cdot \vec{\nabla}$ is the surface gradient operator. On the surface, $\tilde{\Omega}$, there is

$$\vec{\nabla} \cdot \vec{u} = \vec{\nabla}_S \cdot \vec{u} + \vec{n}\vec{n} : \vec{\nabla} \vec{u} \quad (20)$$

Substituting Eq. (1) into Eq. (20), one obtains

$$\vec{n}\vec{n} : \vec{\nabla} \vec{u} = \vec{n}\vec{n} : \langle \varepsilon \rangle = \vec{\nabla} \cdot \vec{u} - \vec{\nabla}_S \cdot \vec{u} \quad (21)$$

In an elastic solid, the constitutive relations of Eq. (2) can be written in the following form

$$\langle \sigma \rangle = \lambda \in \langle I \rangle + 2G \langle \varepsilon \rangle - \frac{\Omega CE}{3(1-2\nu)} \langle I \rangle \quad (22)$$

where λ is the Lamé constant. Using Eqs. (21) and (22), the normal stress component (σ_n) on the surface $\tilde{\Omega}$ can be expressed as

$$\sigma_n = 3 \frac{1-\nu}{1+\nu} \sigma - 2G \vec{\nabla}_S \cdot \vec{u} - \frac{\Omega CE}{3(1-2\nu)} \quad (23)$$

The displacement vector on the surface can be decomposed to as

$$\vec{u} = u_n \vec{n} + u_S \vec{t} \quad (24)$$

where u_n and u_S are the local normal displacement and tangent displacement, respectively. Substituting Eq. (24) in Eq. (23), one obtains

$$\sigma_n = 3 \frac{1-\nu}{1+\nu} \sigma - 2G \vec{\nabla}_S \cdot (u_S \vec{t}) - 2\mu u_n \kappa - \frac{\Omega CE}{3(1-2\nu)} \quad (25)$$

where $\kappa = \vec{\nabla}_S \cdot \vec{n}$ is twice the mean curvature of the undeformed surface. The normal stress is a function of the hydrostatic stress, the tangential displacement component, and the normal component of the surface displacement. Clearly, the undeformed morphology of the solid surface plays an important role in determining the normal stress component to which both the tangent component of displacement vector and the mean curvature contribute. For an initial flat surface, $\kappa = 0$, Eq. (25) reduces to

$$\sigma_n = 3 \frac{1-\nu}{1+\nu} \sigma - 2G \vec{\nabla}_S \cdot (u_S \vec{t}) - \frac{\Omega CE}{3(1-2\nu)} \quad (26)$$

3. Development of chemical stresses in a thin plate

Consider a thin plate of isotropic material in the region $-a \leq x \leq a$, as shown in Fig. 1. Differing from the cases as studied by Li [2], both the surfaces of the plate are constrained in both y and z directions, while no stresses are applied to the surfaces in the x direction. The surface concentrations of solute on both surfaces are maintained only as a function of time, independent of the spatial variables. Driven by the gradient of chemical potential, solute atoms diffuse from both surfaces into the material. Eqs. (12) and (17) become

$$\frac{\partial^2}{\partial x^2} (\sigma + \alpha C) = 0 \quad (27)$$

$$D_0 \left[\frac{\partial^2 C}{\partial x^2} - \frac{\Omega}{RT} \frac{\partial C}{\partial x} \cdot \frac{\partial \sigma}{\partial x} - \frac{\Omega C}{RT} \frac{\partial^2 \sigma}{\partial x^2} \right] = \frac{\partial C}{\partial t} \quad (28)$$

Due to the in-plane symmetry about the y and z axes, there is

$$\sigma_{yy} = \sigma_{zz} \quad (29)$$

On both the surfaces of the plate, there are

$$\sigma_{xx} = 0 \quad \text{at } x = \pm a \quad (30)$$

$$u_S = 0 \quad \text{at } x = \pm a \quad (31)$$

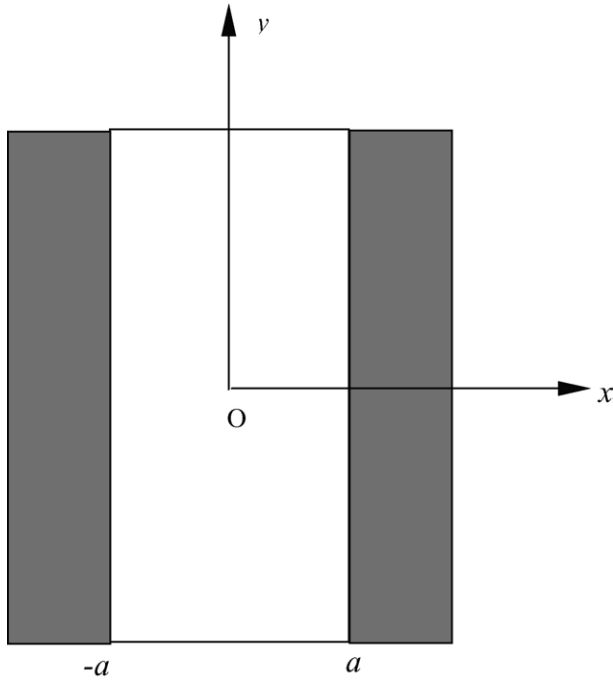


Fig. 1. Schematic diagram of a thin plate subjected to chemical stresses with boundary conditions of $\sigma_{xx} = 0$ and $u_S = 0$ at $x = \pm a$.

Using Eqs. (26) and (31), one obtains the hydrostatic stress on the surfaces as

$$\sigma = \frac{1+\nu}{9(1-\nu)} \frac{E\Omega C}{1-2\nu} \quad \text{at } x = \pm a \quad (32)$$

Based on Eqs. (27) and (32), the relationship between the hydrostatic stress and the concentration can be obtained as

$$\sigma = -\frac{2E\Omega C}{9(1-\nu)} + \frac{E\Omega(C_2 - C_1)}{6(1-2\nu)} \frac{x}{a} + \frac{E\Omega(C_2 + C_1)}{6(1-2\nu)} \quad (33)$$

for $-a \leq x \leq a$

where $C_1 = C|_{x=-a}$ and $C_2 = C|_{x=a}$. As expected, the hydrostatic stress is a linear function of the concentration of solute atoms in the material.

In the following, we only consider several special cases.

3.1. Steady state chemical stresses with constant surface concentrations

Introduce the dimensionless variable, $\tilde{x} = x/a$. Under the condition of constant surface concentration, the steady state diffusion equation is

$$\frac{\partial^2 C}{\partial \tilde{x}^2} - \frac{\Omega}{RT} \frac{\partial C}{\partial \tilde{x}} \cdot \frac{\partial \sigma}{\partial \tilde{x}} - \frac{\Omega C}{RT} \frac{\partial^2 \sigma}{\partial \tilde{x}^2} = 0 \quad (34)$$

Substituting Eq. (33) into Eq. (34), one obtains

$$\left(1 + \frac{\alpha\Omega C}{RT}\right) \frac{\partial^2 C}{\partial \tilde{x}^2} + \frac{\alpha\Omega}{RT} \left(\frac{\partial C}{\partial \tilde{x}}\right)^2 - \frac{\beta\Omega}{RT} \frac{\partial C}{\partial \tilde{x}} = 0 \quad (35)$$

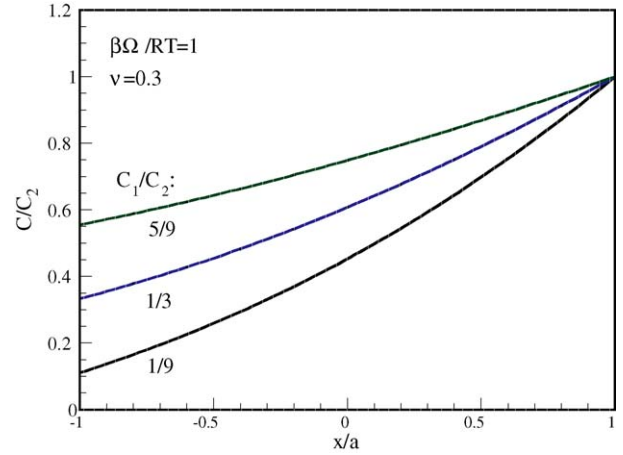


Fig. 2. Distribution of the concentration in the plate for different ratios of surface concentrations ($\beta\Omega/RT = 1$).

where $\beta = E\Omega(C_2 - C_1)/6(1 - 2\nu)$. The analytical solution of Eq. (35) for $C_1 \neq C_2$ is

$$\frac{4}{3} \frac{1-2\nu}{1-\nu} \frac{C}{C_2 - C_1} + \frac{RT}{\beta\Omega} \left(1 - b_1 \frac{4}{3} \frac{1-2\nu}{1-\nu} \frac{C}{C_2 - C_1}\right) \times \ln \left(b_1 + \frac{\beta\Omega C}{RT}\right) = \tilde{x} + b_2 \quad (36)$$

in which b_1 and b_2 are constants to be determined by the boundary conditions.

Using $\nu = 0.3$, the distribution of concentration in the plate is shown in Fig. 2 for different ratios of surface concentrations. Nonlinear distribution of concentration is observed, which is consistent with the numerical calculation given by Simon [21]. The result is different from that given by Zhang et al. [18], since they did not consider the coupling effect in their work. The interaction between diffusion and chemical stresses strongly influences the diffusion of solute atoms and the distribution of solute in materials. The dependence of the distribution of concentration on the parameter, $\beta\Omega/RT$, is depicted in Fig. 3. Larger $\beta\Omega/RT$ introduces more severe nonlinear distribution of

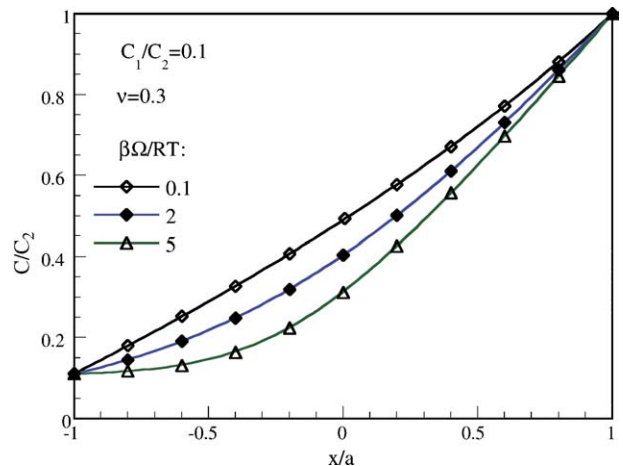


Fig. 3. Distribution of the concentration in the plate for different ratios of $\beta\Omega/RT = 1$ ($C_1/C_2 = 0.1$).

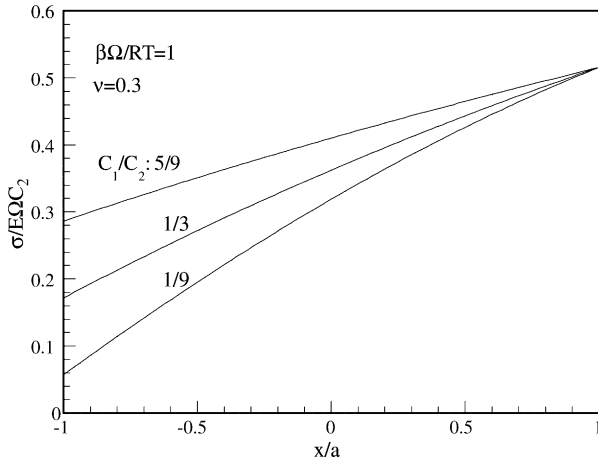


Fig. 4. Istration of the hydrostatic stress in the plate for different ratios of surface concentrations ($\beta\Omega/RT = 1$).

solute atoms in the plate, which plays a great role in determining the evolution of chemical stresses. As expected, the concentration in the plate is a linear function of the spatial variable when $\beta\Omega/RT = 0$. Subjected to the same surface concentrations, the concentration of solute atoms for larger $\beta\Omega/RT$ is less than that for smaller $\beta\Omega/RT$, suggesting that smaller local dilatation is introduced due to faster diffusion for larger $\beta\Omega/RT$.

The profiles of the hydrostatic stress for different C_1/C_2 are plotted in Fig. 4. The plate is subjected to tensile stress due to the diffusion of solute. The chemical stress increases with the ratio C_1/C_2 , with both the maximum and minimum stresses occurs on the surfaces of the plate. A nonlinear distribution of the hydrostatic stress is observed across the plate. To reduce the effect of chemical stresses on the deformation of the plate, it needs to reduce the difference of surface concentrations.

Consider the evolution of stress introduced by the diffusion of boron in polycrystalline silicon. Boron in particular has a solubility of 3×10^{26} atoms/m³ at 900 °C [22]. The partial molar volume of boron in silicon at room temperature is 5.6×10^{-30} m³/atom [1], and the elastic constants of polysilicon are $E = 107$ GPa and $\nu = 0.27$ [23]. It is reasonable to assume that the partial molar volume of boron in silicon at high temperature is approximately equal to 5.6×10^{-30} m³/atom. Using Eq. (32), one obtains a value of 77.67 MPa for the maximum possible hydrostatic stress developed at the silicon interface as a result of diffusion-induced stress.

3.2. Evolution of chemical stresses

Consider the evolution of chemical stresses in the thin plate under the condition that the surface concentrations on both surfaces are same ($\beta = 0$). To determine the distribution of the concentration and the evolution of chemical stresses, we introduce the following dimensionless parameters, $\tilde{t} = D_0 t/a^2$, $\tilde{C} = C/C_0$ and $\tilde{\alpha} = \alpha\Omega C_0/RT$ for constant surface concentration or $\tilde{C} = C/C_{\text{average}}$ and $\tilde{\alpha} = \alpha\Omega C_{\text{average}}/RT$ for a fixed amount of solute deposited initially on the surfaces (C_{average} : the average concentration over the thin plate). Thus, the diffusion

equation becomes

$$(1 + \tilde{\alpha}\tilde{C}) \frac{\partial^2 \tilde{C}}{\partial \tilde{x}^2} + \tilde{\alpha} \left(\frac{\partial \tilde{C}}{\partial \tilde{x}} \right)^2 = \frac{\partial \tilde{C}}{\partial \tilde{t}} \quad (37)$$

Using finite difference approach, Eq. (37) can be approximated by the following finite difference equation,

$$(1 + \tilde{\alpha}\tilde{C}_n^{\tilde{t}_m}) \frac{\tilde{C}_{n+1}^{\tilde{t}_m} - 2\tilde{C}_n^{\tilde{t}_m} + \tilde{C}_{n-1}^{\tilde{t}_m}}{(\Delta\tilde{x})^2} + \tilde{\alpha} \left(\frac{\tilde{C}_{n+1}^{\tilde{t}_m} - \tilde{C}_{n-1}^{\tilde{t}_m}}{2\Delta\tilde{x}} \right)^2 = \frac{\tilde{C}_n^{\tilde{t}_m + \Delta\tilde{t}} - \tilde{C}_n^{\tilde{t}_m}}{\Delta\tilde{t}} \quad (38)$$

where $\tilde{C}_n^{\tilde{t}_m}$ corresponds to the concentration at the position $\tilde{x} = \tilde{x}_n$ and time $\tilde{t} = \tilde{t}_m$, $\Delta\tilde{x} = \tilde{x}_{n+1} - \tilde{x}_n$ and $\Delta\tilde{t} = \tilde{t}_{m+1} - \tilde{t}_m$. The distribution of the concentration in the thin plate as a function of time then can be obtained as

$$\tilde{C}_n^{\tilde{t}_m + \Delta\tilde{t}} = \tilde{C}_n^{\tilde{t}_m} + \Delta\tilde{t} \left[(1 + \tilde{\alpha}\tilde{C}_n^{\tilde{t}_m}) \frac{\tilde{C}_{n+1}^{\tilde{t}_m} - 2\tilde{C}_n^{\tilde{t}_m} + \tilde{C}_{n-1}^{\tilde{t}_m}}{(\Delta\tilde{x})^2} + \tilde{\alpha} \left(\frac{\tilde{C}_{n+1}^{\tilde{t}_m} - \tilde{C}_{n-1}^{\tilde{t}_m}}{2\Delta\tilde{x}} \right)^2 \right] \quad (39)$$

Due to the property of symmetry, only the diffusion in the half of the plate ($0 \leq \tilde{x} \leq 1$) is analyzed. In the simulation, $\Delta\tilde{x} = 0.01$, $i \leq n \leq 101$ and $m \geq 0$. The surface concentration is given as the boundary conditions.

3.2.1. Constant surface concentration

The profiles of the concentration in the thin plate at different times are plotted in Fig. 5 for different $\tilde{\alpha}$ of 0.01, 0.1 and 1. At the same time and same location in the plate, higher concentration is observed for larger $\tilde{\alpha}$, as expected, since larger $\tilde{\alpha}$ means higher local diffusivity. Faster diffusion from the surfaces leads to higher local concentration. One interesting observation is that, for $\tilde{\alpha} \leq 0.01$, the parameter $\tilde{\alpha}$ almost has no influence on the evolution of concentration, which is consistent with the

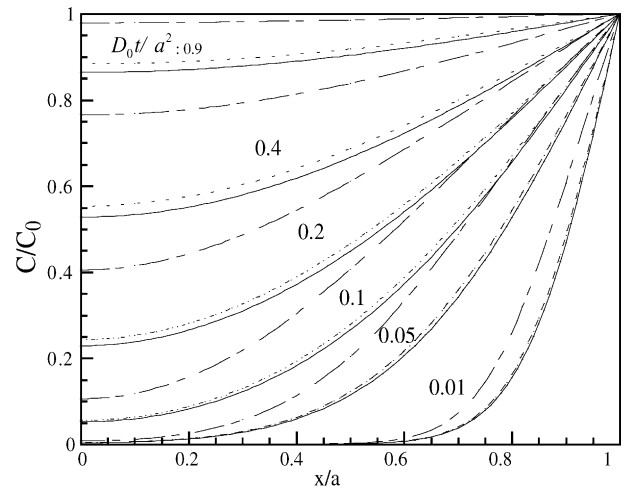


Fig. 5. The concentration distribution in a thin plate of constant surface concentration ((—) $\tilde{\alpha} = 0.01$, (---) $\tilde{\alpha} = 0.1$, (—) $\tilde{\alpha} = 1$).

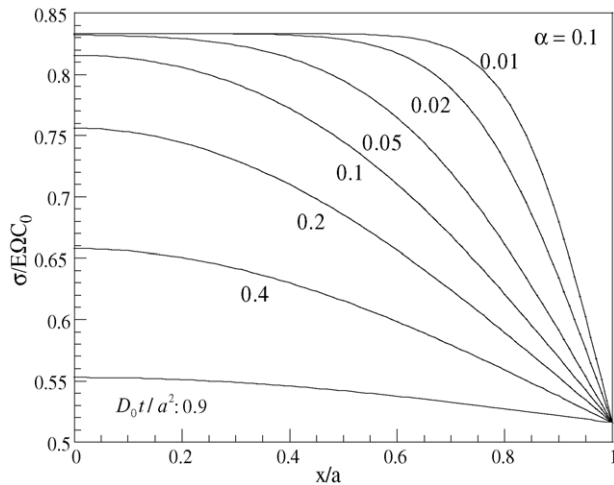


Fig. 6. The evolution of the hydrostatic stress in a thin plate of constant surface concentration ($\tilde{\alpha} = 0.1$).

result given by Chu and Lee [16] in their study of the effect of chemical stresses on diffusion under the condition of constant surface chemical potential. The interaction between chemical stresses and diffusion is negligible in the study of diffusion-induced stress and stress-induced diffusion for $\tilde{\alpha} \leq 0.01$.

Using $\nu = 0.3$, the evolution of hydrostatic stress in the plate is depicted in Fig. 6. The plate is subjected to tension due to the constraint, $u_S = 0$. The maximum stress is occurring at the center in the beginning of diffusion, which is different from free-standing plate as discussed by Li [2]. Similar to the result given by Li [2], stresses are present at the center of the plate for a short time of diffusion even though the solute has not diffused to the center of the plate. This suggests that there is no direct correlation between the gradient of concentration and stresses. When uniform distribution of concentration is reached, the hydrostatic stress reaches a constant as given in Eq. (32), which is proportional to the concentration.

3.2.2. Fixed amount of solute deposited initially on the surfaces

The profiles of the concentration in the thin plate at different times are plotted in Fig. 7 for different $\tilde{\alpha}$ of 0.01, 0.1 and 1 under the condition that fixed amount of solute is deposited initially on the surfaces. Near the surfaces, less amount of solute is found for larger $\tilde{\alpha}$, while, in the central portion of the plate, larger amount of solute is observed for larger $\tilde{\alpha}$ due to faster diffusion from the surfaces. Similar to the case with constant surface concentration, the parameter $\tilde{\alpha}$ almost has no influence on the evolution of the concentration for $\tilde{\alpha} \leq 0.01$. Eventually, a uniform distribution of concentration is reached, which is independent of the interaction between chemical stresses and diffusion.

The evolution of the hydrostatic stress in the plate for $\nu = 0.3$ is depicted in Fig. 8. The plate is always subjected to tension due to the constraint, $u_S = 0$. The maximum stress is occurring at the center at the beginning of diffusion, which is different from free-standing plate as discussed by Li [2]. Similar to the result given by Li [2], stresses are present at the center of the plate for a short time of diffusion even though the solute has not diffused to the

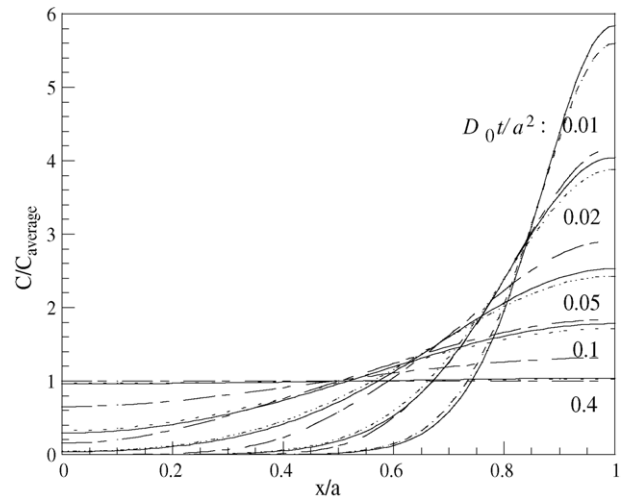


Fig. 7. The concentration distribution in a thin plate, having fixed amount of solute deposited initially on the surfaces ((—) $\tilde{\alpha} = 0.01$, (---) $\tilde{\alpha} = 0.1$, (---) $\tilde{\alpha} = 1$).

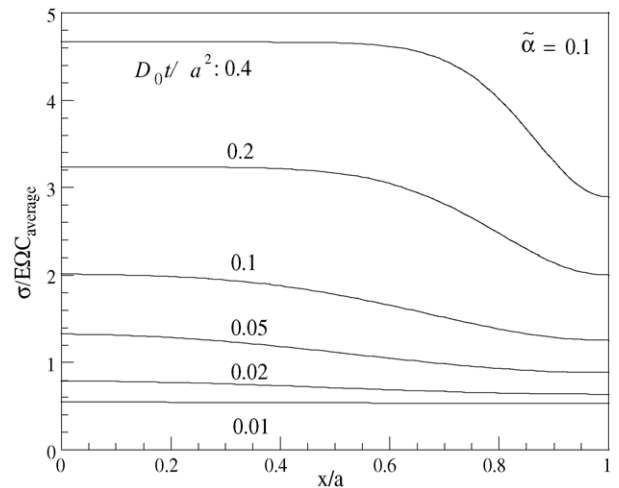


Fig. 8. The evolution of the hydrostatic stress in a thin plate, having fixed amount of solute deposited initially on the surfaces ($\tilde{\alpha} = 0.1$).

center of the plate. This is consistent with the finding in above section that there is no direct correlation between the gradient of concentration and stresses. Much higher stress is developed at the beginning than that having a constant surface concentration. The stresses developed in the plate decrease with time and reach constant values once uniform distribution of concentration is reached.

4. Summary

The interaction between chemical stresses and diffusion has been investigated by assuming a linear relation between the diffusion-induced strain and the concentration of solute. Following the approach used in the theory of linear elasticity, it is found that the hydrostatic stress being a harmonic function is dependent upon the concentration. For a solid free of the action of body force, the Laplacian of the hydrostatic stress is proportional to the Laplacian of the concentration of solute, that is,

deviation of the hydrostatic stress from its local average is proportional to deviation of the local concentration of solute. Based on the approximation of small deformation, the normal stress developed over the surface of a solid is dependent on the mean curvature of the undeformed surface and tangential components of the surface displacement. Using the new relationships, the evolution of chemical stresses in a thin plate is discussed. For a plate subjected to the constraint ($u_S = 0$) over the surface, a closed-form solution of the steady state concentration of solute is obtained. It turns out that nonlinear distribution of solute in the plate is existent due to the interaction between chemical stresses and diffusion.

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