

A HIGHER-ORDER GRADIENT DIFFUSION THEORY

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ABSTRACT

This paper presents a one-dimensional higher-order gradient (HOG) theory of atomic diffusion. It is assumed that the diffusion flux is linearly related not only to the first but also to the higher order concentration gradients of diffusing atoms. A length parameter is introduced in the HOG theory to account for the size effects when diffusion occurs at different length scales. A simple example of one-dimensional, steady-state diffusion is given to examine the effect of higher-order gradients on the concentration distribution of diffusing atoms.

Keywords: Diffusion; Fick's law; gradient theory

1. INTRODUCTION

Atomic diffusion is an important phenomenon that influences mechanical and thermal properties of materials. Atomic diffusion and more general mass transport have been studied using Fick's first and second laws [1, 2]. According to Fick's first law, the flux of diffusing matter, or the flow of matter crossing a unit area per unit time J , is linearly related to the concentration gradient as follows

$$J = -D \frac{\partial C}{\partial x} \quad (1)$$

where C is the concentration of diffusing matter, D the diffusion coefficient and x the diffusion direction. When applied to atomic diffusion, C represents the concentration of diffusing atoms. The time dependence of diffusion is governed by Fick's second law

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

where t is time.

Fick's laws constitute a phenomenological theory of mass transport. While Fick's first law is applicable to mass flow at small (e.g., atomic and microscopic) scales, it lacks a length parameter to explore influences of characteristic lengths (for example, atomic spacing and grain size), or the size effects in diffusion processes. Moreover, a length parameter is also needed to describe diffusion phenomena occurring at different length scales. The size effects may be ignored when the characteristic lengths are much smaller than the diffusion distances. When diffusion distances are comparable to a characteristic length, size effects may become significant and classical Fick's laws may not be able to accurately predict the diffusion profiles and fluxes. Examples include diffusion in nanomaterials, microelectronic devices and thin films. Here we propose a one-dimensional higher-order gradient (HOG) theory for atomic diffusion by including higher order gradients of concentration in Fick's first law. A length parameter naturally arises in the HOG theory thereby making it possible to explore size effects and to bridge the diffusion processes at different length scales.

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2. EFFECTS OF HIGHER ORDER GRADIENTS

To derive the governing equations in the HOG theory, or modified Fick's laws, we first consider atomic diffusion between two crystallographic planes as shown in Figure 1. It has been known that the flux of atoms, J , in a simple cubic crystal is related to the concentration difference between the two atomic planes by [1, 2]

$$J = -\frac{\nu a}{6} \Delta C \quad (3)$$

where ν is the jump frequency of atoms, a the lattice constant, and $\Delta C = C_{x+\Delta x} - C_x$ the difference between concentrations of the diffusing atoms at the two adjacent atomic planes. In the classical diffusion theory, ΔC is approximated using the differential $(\partial C / \partial x)\Delta x$. Here, we use the Taylor series truncated at the third term to obtain an approximate expression for DC with the result

$$\Delta C = \frac{\partial C}{\partial x} \Delta x + \frac{1}{2} \frac{\partial^2 C}{\partial x^2} (\Delta x)^2 + \frac{1}{6} \frac{\partial^3 C}{\partial x^3} (\Delta x)^3 \quad (4)$$

We note that an expansion similar to (4) was given in [3] which was mainly on the finite difference equation from an atomistic model of diffusion and a higher-order gradient theory was not pursued. In atomic diffusion, x may be regarded as the lattice parameter a . Substituting the above equation into Eq. (3), we have

$$J = -D \left(\frac{\partial C}{\partial x} + \frac{a}{2} \frac{\partial^2 C}{\partial x^2} + \frac{a^2}{6} \frac{\partial^3 C}{\partial x^3} \right) \quad (5)$$

where D is the diffusion coefficient given by

$$D = \frac{\nu a^2}{6} \quad (6)$$

Eq. (5) is a modified Fick's first law for simple cubic materials. In this HOG theory, the diffusion flux is linearly related to the first order concentration gradient $\partial C / \partial x$ as well as the second and third order concentration gradients of diffusing atoms.

In general, the relationship between the flux and concentration gradients of diffusing atoms may be expressed as

$$J = -D \left(\frac{\partial C}{\partial x} + l \frac{\partial^2 C}{\partial x^2} + \alpha l^2 \frac{\partial^3 C}{\partial x^3} \right) \quad (7)$$

where l is a length parameter and α a dimensionless parameter. When applied to atomic diffusion, we may assume $l = a/2$ and $\alpha = 2/3$ for simple cubic crystals. For fcc and bcc materials, $l = a/4$ and $\alpha = \sqrt{2/3}$ where a is the lattice constant. The HOG theory reduces to Fick's first law when $l \rightarrow 0$.

Eq. (7) represents a kind of constitutive relation for solid state diffusion. The $\partial^2 C / \partial x^2$ term in Eq. (7) is not invariant under the $x \rightarrow -x$ transformation in the final equation for C and therefore will be dropped for materials that possessing the invariance. The proposed modification on Fick's first law thus becomes

$$J = -D \left(\frac{\partial C}{\partial x} + \alpha l^2 \frac{\partial^3 C}{\partial x^3} \right) \quad (8)$$

By using the modified Fick's first law, Eq. (8), and conservation of matter, the basic governing equation in the HOG theory of diffusion can be obtained as follows

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \alpha l^2 \frac{\partial^4 C}{\partial x^4} \right) \quad (9)$$

Eqs. (8) and (9) are modified Fick’s first and second laws, respectively. Coleman and Mizel [4] proposed similar but more general modifications of Fourier’s law and heat conduction equations which have the same mathematical forms as Fick’s laws in the classical theories.

When using Eqs. (8) and (9) to study time-dependent concentration fields, appropriate initial and boundary conditions are required. Eq. (9) is a fourth-order partial differential equation that requires two boundary conditions at a boundary, which is opposed to the classical diffusion theory in which only one condition is needed at a boundary. Here we attempt to gain an insight into mathematically and physically admissible boundary conditions for the HOG theory using a weighted residual method. Consider diffusion in an interval $0 \leq x \leq L$. The weighted residual equation of the HOG theory is

$$\int_0^L W \left[\frac{\partial C}{\partial t} - D \left(\frac{\partial^2 C}{\partial x^2} + \alpha l^2 \frac{\partial^4 C}{\partial x^4} \right) \right] dx = \int_0^L W \left[\frac{\partial C}{\partial t} + \frac{\partial J}{\partial x} \right] dx = 0 \tag{10}$$

where W is a weight function. Using integration by parts yields

$$(WJ)_0^L + \left[\frac{\partial W}{\partial x} D \left(C + \alpha l^2 \frac{\partial^2 C}{\partial x^2} \right) \right]_0^L + \int_0^L \left[W \frac{\partial C}{\partial t} - \frac{\partial^2 W}{\partial x^2} D \left(C + \alpha l^2 \frac{\partial^2 C}{\partial x^2} \right) \right] dx = 0 \tag{11}$$

Possible natural boundary conditions on a boundary may be formulated from the above weighted residual equation as follows

$$C + \alpha l^2 \frac{\partial^2 C}{\partial x^2} = \bar{H} \quad \text{or} \quad J = \bar{J} \tag{12}$$

where \bar{H} and \bar{J} are prescribed values. Besides the above natural boundary conditions, the essential boundary condition is

$$C = \bar{C} \tag{13}$$

where \bar{C} is the prescribed concentration on a boundary. Eqs. (12) and (13) indicate that the second-order derivative of concentration may be prescribed on a boundary. This boundary condition is mathematically consistent with those in the gradient theory of electric field [5]. We note that further efforts are needed to explore the physics of the boundary condition (12). In general, the concentration C and the flux J may not be prescribed simultaneously on a boundary.

3. AN EXAMPLE

Next, we consider a simple problem of one-dimensional steady-state diffusion in $0 \leq x \leq L$. Under steady-state conditions, the governing diffusion equation (9) reduces to

$$\frac{d^2 C}{dx^2} + \alpha l^2 \frac{d^4 C}{dx^4} = 0 \tag{14}$$

The boundary condition of the problem may be formulated as follows

$$\begin{aligned} C &= C_0, & x &= 0, \\ C &= C_L, & x &= L, \\ \frac{d^2 C}{dx^2} &= \frac{C_0}{L^2} H_0, & x &= 0, \\ \frac{d^2 C}{dx^2} &= \frac{C_0}{L^2} H_L, & x &= L \end{aligned} \tag{15}$$

where C_0 and C_L are prescribed concentration at $x = 0$ and L , respectively, and H_0 and H_L are prescribed, normalized second order derivatives of concentration. The general solution of Eq. (14) is

$$C(x) = b_1 \cos\left(\frac{x}{\sqrt{\alpha} l}\right) + b_2 \sin\left(\frac{x}{\sqrt{\alpha} l}\right) + b_3 \frac{x}{L} + b_4 \quad (16)$$

where b_i ($i = 1, 2, 3, 4$) are constants to be determined by the boundary conditions. Substituting Eq. (16) into the boundary conditions (15) yields the following equations for b_i

$$\begin{aligned} b_1 + b_4 &= C_0, \\ C_{al} b_1 + S_{al} b_2 + b_3 + b_4 &= C_L, \\ b_1 &= -\alpha (l/L)^2 C_0 H_0, \\ C_{al} b_1 + S_{al} b_2 &= -\alpha (l/L)^2 C_0 H_L \end{aligned} \quad (17)$$

where

$$C_{al} = \cos\left(\frac{L}{\sqrt{\alpha} l}\right), \quad S_{al} = \sin\left(\frac{L}{\sqrt{\alpha} l}\right) \quad (18)$$

Solving Eq. (18) for b_i , we have

$$\begin{aligned} b_1 &= -\alpha (l/L)^2 C_0 H_0, \\ b_2 &= \alpha (l/L)^2 C_0 (H_0 C_{al} - H_L) / S_{al}, \\ b_3 &= C_L - C_0 + \alpha (l/L)^2 C_0 (H_L - H_0), \\ b_4 &= C_0 + \alpha (l/L)^2 C_0 H_0 \end{aligned} \quad (19)$$

Substituting Eq. (19) into Eq. (16) yields the concentration field

$$\begin{aligned} C(x) &= -\alpha (l/L)^2 C_0 H_0 \cos\left(\frac{x}{\sqrt{\alpha} l}\right) + \alpha (l/L)^2 C_0 (H_0 C_{al} - H_L) \sin\left(\frac{x}{\sqrt{\alpha} l}\right) / S_{al} \\ &+ [C_L - C_0 + \alpha (l/L)^2 C_0 (H_L - H_0)] \frac{x}{L} + C_0 [1 + \alpha (l/L)^2 H_0] \end{aligned} \quad (20)$$

The above solution of the HOG theory reduces to the following classical solution

$$C(x) = (C_L - C_0) \frac{x}{L} + C_0 \quad (21)$$

when l goes to zero.

As a numerical example, we consider atomic diffusion in fcc materials, for example, diffusion of copper in nickel. In all calculations, H_0 and H_L are taken to be 1.0. Figure 2 shows the nondimensional concentration of diffusing atoms, C/C_0 , versus x/L responses for various values of the dimensionless length parameter L/l . The concentration ratio C_L/C_0 is taken as zero. The classical solution is also included. It is seen from the figure that when $L/l = 2.0$, i.e., the diffusion distance is comparable to the scale length in the HOG theory, the concentration distribution of the HOG theory deviates significantly from that of the classical theory, especially in the middle part of the diffusion domain. When the diffusion distance increases to 10 times the scale length l , the HOG solution reduces to the classical solution.

4. CONCLUSION

A higher-order diffusion theory is proposed. It generalizes Fick's first law by including the effects of higher order gradients of the concentration of the diffusing matter. Mathematically the proposed theory results in a fourth-order

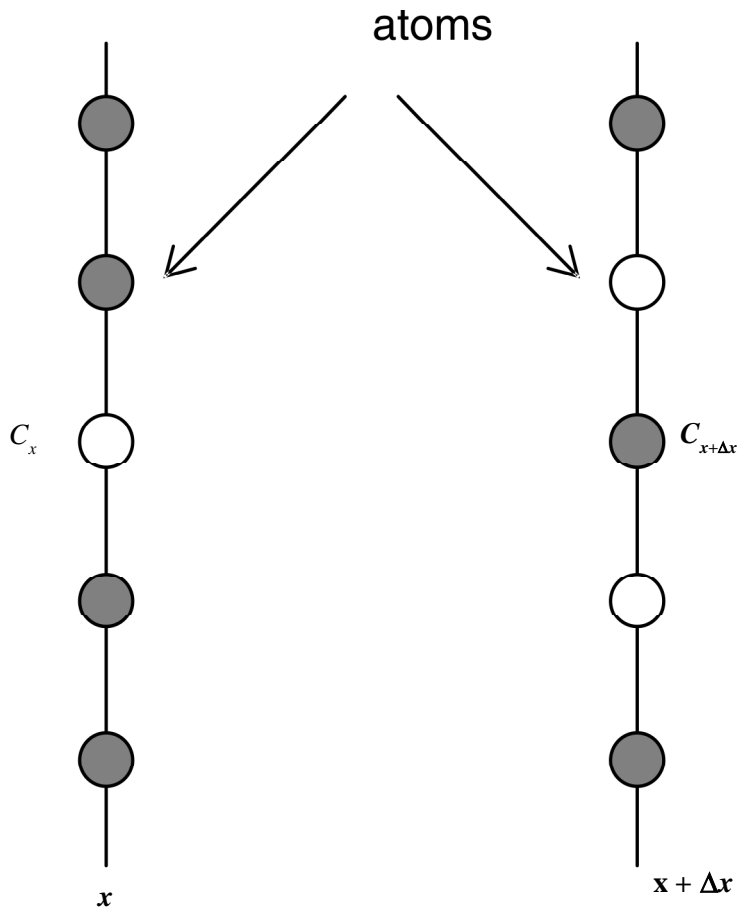


Figure 1: Atomic Diffusion between Two Crystallographic Planes

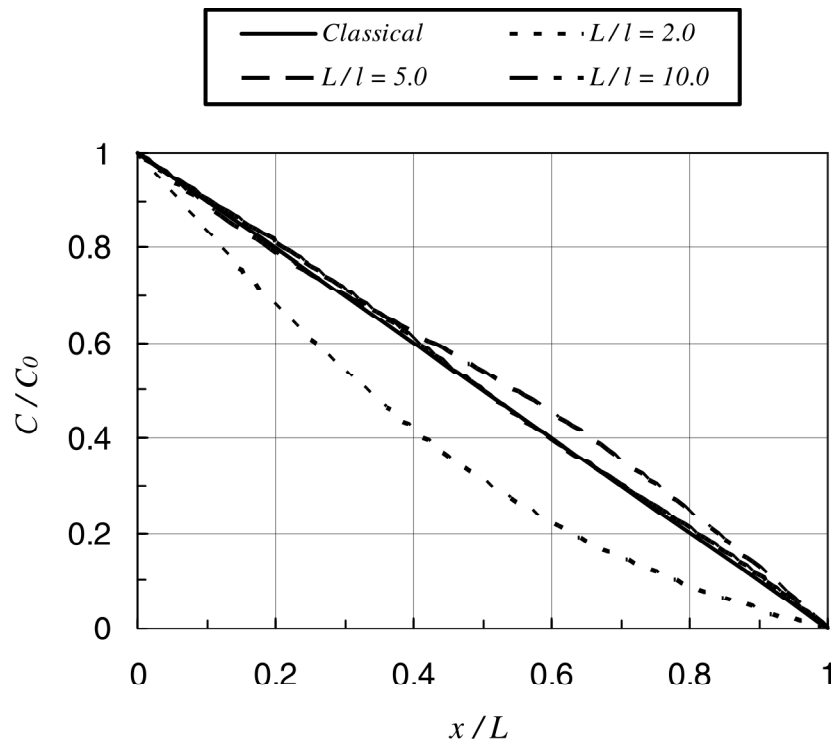


Figure 2: Concentration Distributions for Various Values of L/l

partial differential equation. It contains new material parameters and can describe size-dependent effects in diffusion. Numerical results show that the concentration distribution of the HOG theory deviates from that in the classical diffusion theory when the diffusion range is comparable to the scale length. The HOG theory solution reduces to the classical solution when diffusion distances become at least one order of magnitude larger than the scale length. The present work focuses on the one-dimensional theory. The three-dimensional theory will be pursued in the future study.

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