Three Methods for Solution of Concentration Dependent Diffusion Coefficient

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Abstract

This study offers three analytical solutions of the diffusion coefficient's dependence on concentration in general cases without any limitations by boundary conditions. They are all suitable for numerical analysis when the experimental concentration data and time series are available producing dependence functions. As they are also of general nature, the expressions can be used for further analytical investigations and analytical modeling and fitting. Two of the methods offer three-dimensional approaches to this problem and may prove useful when combined with present-day laser scanning volumetric sensors, atomic probe microscopes and high performance computers. This is particularly true in geometries more complex than the regular one consisting of two semi-infinite slabs. [1][2]

0.1 Keywords

diffusion, nonlinear diffusion, concentration dependence, diffusion of solids

1 Introduction

The concentration dependence is of importance in studying impurity diffusion in metals and semiconductors at high temperatures but will find applications in other fields of diffusion as well. E.g. finding sudden changes in concentration dependence may reveal changes in crystal structure in alloys. This paper handles in a short and communicative way three analytical methods for solving the behavior of concentration dependence of the diffusion coefficient from experimental data. The first one is a general integral formula in three dimensions giving a good platform for further analytical investigations. The second one is

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[1] Visilab Report #2004-03. Revision 3, 01-10-2011. First published in June 2004. Minor typographical corrections made and written in LaTeX.

also an integral expression of a more complicated and general nature but being better suited for numerical analysis. The third method is for one-dimensional problems being also an integral expression suitable for numerical analysis. All results are carried out using rather elementary analysis.

1.1 Statement of Problem and History

The problem of diffusion coefficients depending on concentration has been known as a fact for a long time through experimental data. The purpose is to solve the dependence from the experimental concentration values measured at varying locations and times. The typical geometry is a simple two-material boundary with simple natural boundary conditions. The acquired data are usually in a form not too suitable for numerical work as the differences in concentration as a function of time are small. Theoretically, the diffusion equation is known to be hard to solve in analytical form, in spite of its simplicity, if there is any nonlinearity, no matter how trivial it be. That builds a strong wall against modeling and experimenting in analytical and numerical terms. Only with some special boundary conditions have some simple cases been given any reasonable form as the solution. Brute force numerical solutions are, of course, possible, but require careful analysis of boundary conditions and are cumbersome to perform if parametric behavior is to be studied. An introductory discussion is in Shewmon [3]. The available work made by pioneers, like Boltzmann [1] and Matano [2], lend little hand to further analytical studies.

1.2 Method of Boltzmann

Ludwig Boltzmann [1] studied the one-dimensional diffusion equation below with the aid of a simple change of variable Equation (1). The original problem was that of diffusion of two fluids measured with the aid of light to see the change in index of refraction in both media. The resulting equations are one-dimensional.

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x}(k \cdot \frac{\partial n}{\partial x}) \tag{1}$$

k is the diffusion coefficient being a function of index n of the resulting mixture of fluids at various distances x.

$$\lambda = \frac{x}{\sqrt(t)} \tag{2}$$

After integration, one obtains for constant t

$$k(n) = \frac{1}{2 \cdot t \cdot \frac{dn}{dx}} \cdot \int_x^\infty \frac{dn}{dx} \cdot x \cdot dx \tag{3}$$

This result is dependent on the simple boundary conditions.

1.3 Method of Matano

The method of Chujiro Matano [2] is based on similar mathematics as Boltzmann. His special boundary conditions for the concentration equation (4) were:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}(D(c) \cdot \frac{\partial c}{\partial x}) \tag{4}$$

$D(c)$ is the diffusion coefficient being a function of c. At $t = 0$

$$c = 1, \ when \ x > 0 \tag{5}$$

and

$$c = 0, \ when \ x < 0 \tag{6}$$

and always at $x = \pm\infty$

$$\frac{\partial c}{\partial x} = 0 \tag{7}$$

With the identical substitution Equation (2) as above we get for the diffusion equation

$$-\frac{\lambda}{2} \cdot \frac{dc}{d\lambda} = \frac{\partial}{\partial \lambda} \cdot (D \cdot \frac{dc}{d\lambda}) \tag{8}$$

With the boundary conditions this can be solved.

$$D(c) = -\frac{1}{2} \cdot \frac{d\lambda}{dc} \cdot \int_0^c \lambda \cdot dc \tag{9}$$

having also the condition

$$\int_0^1 \lambda \cdot dc = 0 \tag{10}$$

When $t = constant$ we get

$$D(c) = \frac{1}{2 \cdot t} \cdot \frac{dx}{dc} \cdot \int_c^1 x \cdot dc \tag{11}$$

with

$$\int_0^1 x \cdot dc = 0 \tag{12}$$

The Equation (11) can be used in numerical methods with carefully observed boundary conditions. The formula is simple and much relies on accuracy of experimental concentration values.

2 Theory

2.1 The First Method

The concentration dependence of the diffusion coefficient can be stated as follows.

$$D = D(c) \tag{13}$$

where c is the concentration and D is the diffusion coefficient having in general some dependence on concentration. The diffusion equation in three dimensions is as follows.

$$\frac{\partial c}{\partial t} = \nabla \cdot (D(c)\nabla c) \tag{14}$$

where t is the time. The basic assumption is to have the knowledge of $c(\bar{r}, t)$ from experimental data as well as

$$\frac{\partial c(\bar{r}, t)}{\partial t} \tag{15}$$

The data is in three dimensions in general and in one dimension in restricted cases. The data series should contain at least some reasonable time range to obtain any practical numerical results for D. The concentration behaves always in a continuous way with some quite natural boundary conditions. Only at $t = 0$ the concentration may have either a piecewise continuous behavior or it may even be discontinuous. However, at times $t > 0$, it behaves continuously and so does its derivatives. We have made some operations in the following which might at first sight seem careless. However, as the derivatives and the functions of them, behave in a continuous manner, there is no reason for alarm. Our task is now to solve $D(c)$ from Equation (14) in a closed analytical form. We start by introducing the simple transformation:

$$\nabla \cdot (D(c)\nabla c) = \nabla^2 F(c) \tag{16}$$

Here $F(c)$ is a scalar function of concentration which is equal to

$$F(c) = \int_{c0}^{c} D(c) \cdot dc \tag{17}$$

and thus Eq.(14) becomes

$$\frac{\partial c}{\partial t} = \nabla^2 \cdot F(c) \tag{18}$$

We know the property of the three-dimensional delta function

$$\nabla^2 (\frac{1}{\bar{r} - \bar{r}_1}) = -4 \cdot \pi \cdot \delta(\bar{r} - \bar{r}_1) \tag{19}$$

and transform the left-hand side of Equation (17) to an integral

$$F(c) = -\frac{1}{4 \cdot \pi} \int \frac{\frac{\partial c(\bar{r}_2, t)}{\partial t}}{(\bar{r} - \bar{r}_2)} d\bar{r}_2 \tag{20}$$

This can be differentiated with respect to c and to obtain $D(c)$

$$D(c) = -\frac{1}{4 \cdot \pi} \frac{\partial}{\partial c} \int \frac{\frac{\partial c(\bar{r}_2, t)}{\partial t}}{(\bar{r} - \bar{r}_2)} d\bar{r}_2 \tag{21}$$

The integral is a function of $\bar{r}$ at a fixed time t and thus a function of c since we know $c(\bar{r}, t)$. The apparent singularity can usually be overcome by a Cauchy principal value when dealing with analytical expressions.

2.2 The Second Method

We use the diffusion equation and other basic relations as before. We can now use the known relation

$$\nabla D(c) = D'(c) \cdot \nabla c \tag{22}$$

Substituting this into Equation (14) one gets

$$\frac{\partial c}{\partial t} = D'(c) \cdot \nabla c^2 + D(c) \cdot \nabla^2 c \tag{23}$$

and a differential equation for $D(c)$

$$D'(c) + D(c) \cdot g(c) = hc \tag{24}$$

Here

$$g(c) = \frac{\nabla^2 c(\bar{r}, t)}{(\nabla c(\bar{r}, t))^2} \tag{25}$$

and

$$h(c) = \frac{\frac{\partial c(\bar{r}, t)}{\partial t}}{(\nabla c(\bar{r}, t))^2} \tag{26}$$

g and h are functions of c only since we know $c = c(\bar{r}, t)$. We can, in principle, solve for $\bar{r}$. Equation (24) is of linear type and it has an immediate solution

$$D(c) = \exp\,(-\int_{c_{00}}^{c} g(c_1) \cdot dc_1) \cdot (\int_{c_0}^{c} \exp\,(\int_{c_{000}}^{c_2} g(c_3) \cdot dc_3) \cdot h(c_2) \cdot dc_2 + D_0) \tag{27}$$

We have used an arbitrary initial condition

$$D(c_0) = D_0 \tag{28}$$

This method is useful when projected to one-dimensional problems.

2.3 The Third Method

The last method is for one-dimensional problems alone. After flattening Equation (14) to one dimension, one can integrate it from x to ∞ and divide it by

$$\frac{\partial c}{\partial x} \tag{29}$$

to get

$$D(c) = \frac{A_0 - \int_x^{\infty} \frac{\partial c(x_1, t)}{\partial t} \cdot dx_1}{\frac{\partial c(x, t)}{\partial x}} \tag{30}$$

Time t is fixed and so we can solve for

$$x = c^{-1}(c(x)) \tag{31}$$

this being more or less trivial in numerical terms with the experimental data. The numerator and the denominator are functions of c only. A_0 can be fixed by the natural boundary condition

$$\lim_{x\to\infty} \frac{\partial c(x,t)}{\partial x} = 0 \quad \Rightarrow A_0 \tag{32}$$

and we have finally

$$D(c) = \frac{\int_x^\infty - \frac{\partial c(x_1,t)}{\partial t} \cdot dx_1}{\frac{\partial c(x,t)}{\partial x}} \tag{33}$$

This result is always valid independent of boundary conditions. As a method of solution for concentration dependence, it is more general than the methods of Boltzmann and Matano.

2.4 Conclusions

These methods offer immediate general solutions (Equations (21), (27) and (33)) for the concentration dependence of the diffusion coefficient being free of any limiting boundary conditions at this time. One has the option of choosing numerically most attractive of these. It should be noted that to obtain results of sufficient accuracy, the coordinate ranges of $\bar{r} = \bar{r}(x, y, z)$ and especially t should be wide enough. Error estimation is outside the scope of this work. The latter two methods are very sensitive to the spatial gradient and thus care in numerical work is required. The results resemble the results of Boltzmann and Matano but have more general boundary conditions and thus wider applications. The methods of Boltzmann and Matano rely on the assumption of simplifying the diffusion equation with the variable $\frac{x}{\sqrt{(t)}}$. In general three-dimensional cases, this is a too strong assumption and is not directly supported by experimental data. The methods developed in this study, make no assumptions in this respect. The two methods with three-dimensional basis offer a good platform for irregular geometries or one may also use curvilinear coordinates in special cases.

References

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