A Numerical Method for the Diffusion Equation with Concentration-Dependent Diffusivity

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Key Questions

- How to adapt existing analytical methods to interdiffusion systems?
- What are the characteristics of solutions with concentration-dependent diffusivity?
- How does the diffusion profile calculated by the present method compare with experimentally fitted data?

Introduction

The diffusion equation is formulated using an interdiffusion coefficient based on Darken's relation, assuming intrinsic diffusivities are proportional to the power of concentration.

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D(c)\frac{\partial c(x,t)}{\partial x}\right) \quad (1)$$

$$D(c) = \tilde{D}(n_A, n_B) = D_{A0}\left(\frac{c_B}{c_0}\right)^{n_A} X_B + D_{B0}\left(\frac{c_A}{c_0}\right)^{n_B} X_A \quad (2)$$

The initial condition and the boundary condition are given in Eqs. (3).

$$c(x>0, t=0) = 0, c(x=0, t\geq 0) = c_0 \quad (3)$$

Equations (1)-(3) are referred to as the diffusion equation with a concentration-dependent diffusion coefficient in a semi-infinite medium.

- **Motivation**: We are trying to solve Eq.(1) by the analytic method Pelton and Estell[1] and Blanc[2] introduced.
- **Challenge**: Analytical solutions for $D(c)$ are limited to only intrinsic diffusion models.
- **Approach**: Developed a numerical approach incorporating previous analytical methods.

Methodology - The Serial Transformation

By applying the serial transformations introduced in previous studies, the partial differential equation can be reduced to the following ordinary differential equation:

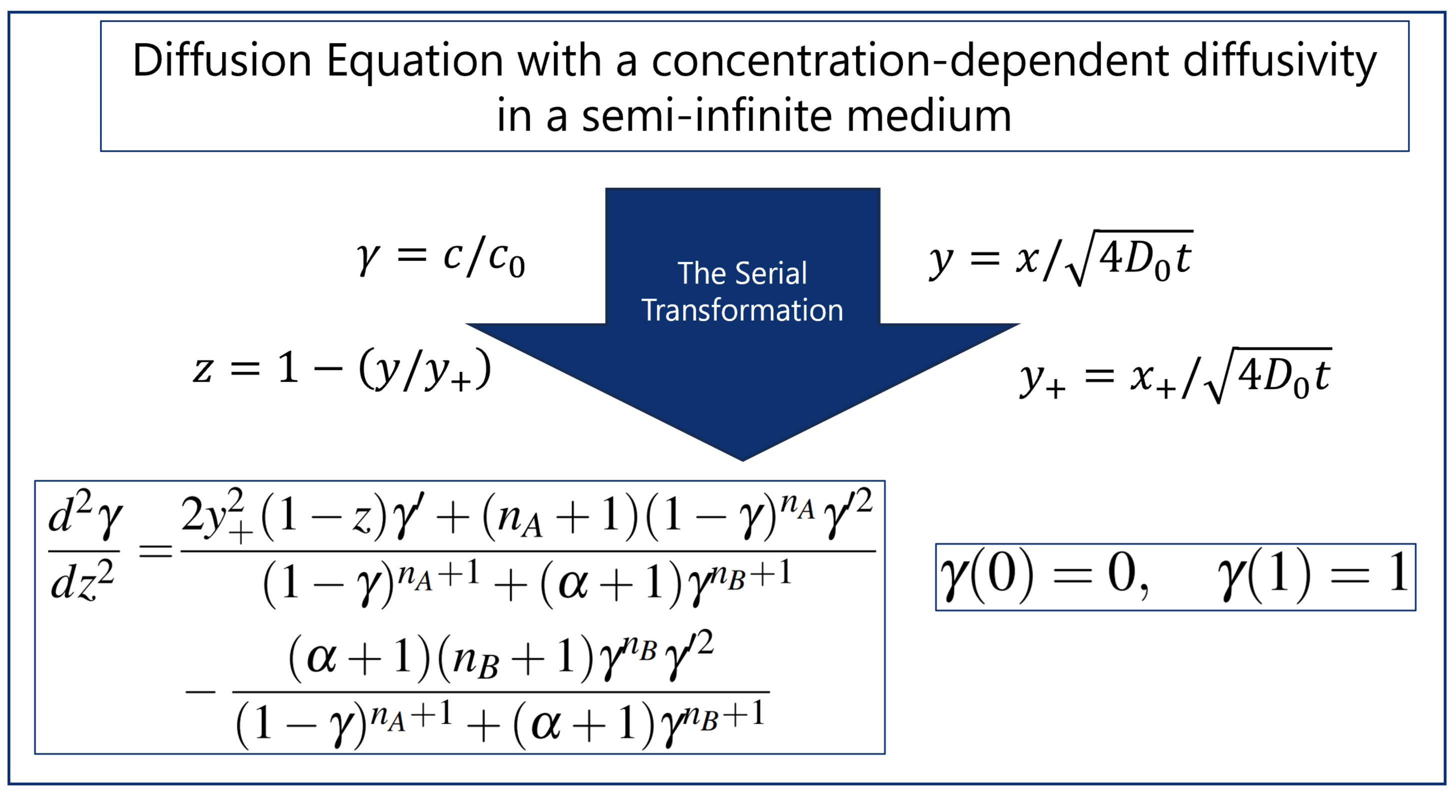

Figure 1. Schematic of the serial transformation

The Boltzmann parameter is $y = x/(4D_0 t)^{0.5}$, Boltzmann parameter at x_+ is $y_+ = x_+/(4D_0 t)^{0.5}$, and x_+ is the position where $c_A = 0$. Here, we assume that the diffusivity of pure B is $(\alpha+1)D_{A0}$ where α is constant.

Methodology - Numerical Details

Solutions were obtained numerically using a two-step iterative procedure, consisting of an inner step that determines the initial slope of the solution via the shooting method and an outer step that verifies the satisfaction of mass conservation. Calculations were conducted by using Python Scipy package. The initial slope s is updated by Brent's method.

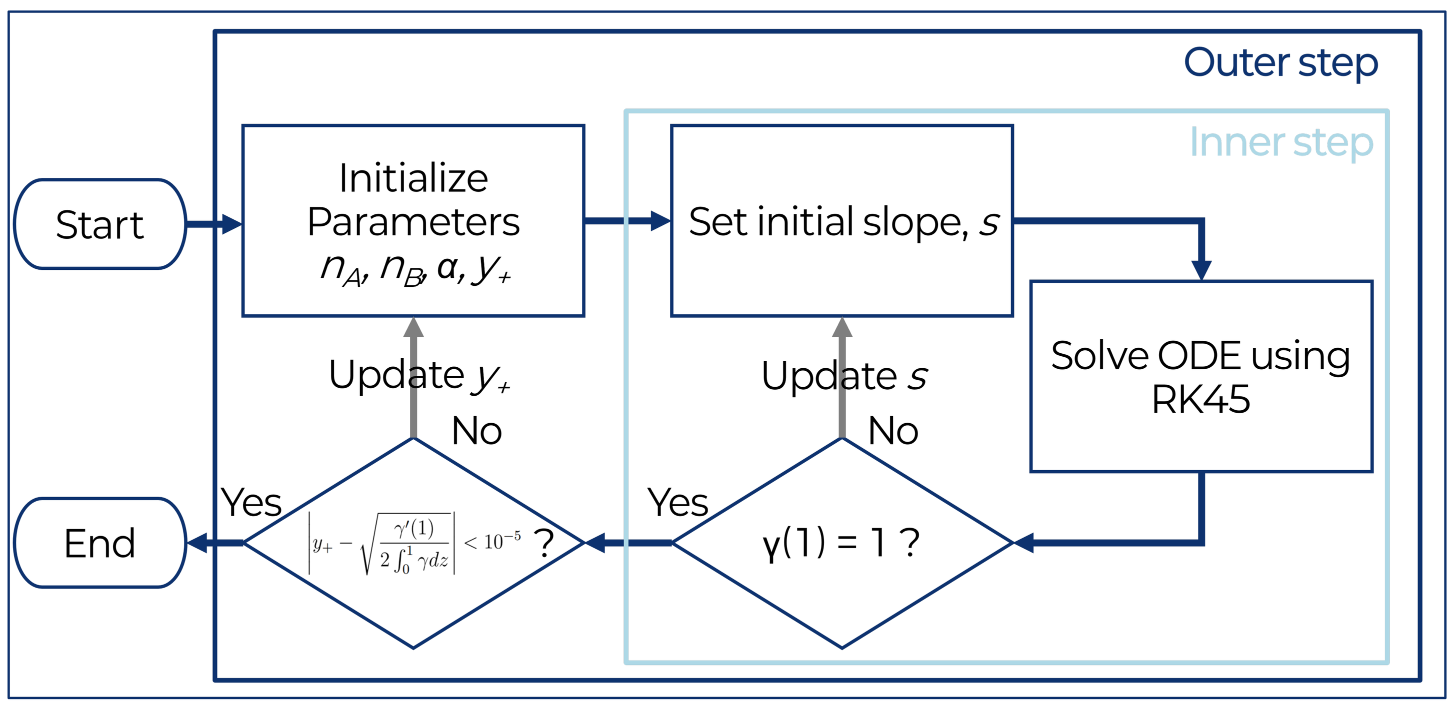

Figure 2. Flowchart of the numerical procedure

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Results - Case 1: Hypothetical Binary Systems

We analyzed the characteristics of solutions to the diffusion equation. Increasing the exponent (either n_A or n_B) leads to a concave-down profile in the high-concentration range and a more pronounced curvature. Moreover, even though the differences in γ are minor (Fig. 3), variations in n_A and n_B lead to pronounced changes in γ'' across different z regions (Fig. 4).

Variations in n_A and n_B lead to pronounced changes in γ'' across different z regions. The distinction in γ'' between cases originates from differences in diffusivity. We discovered that n_A and n_B strongly influence the solution behavior of the diffusion equation with chemical diffusivity.

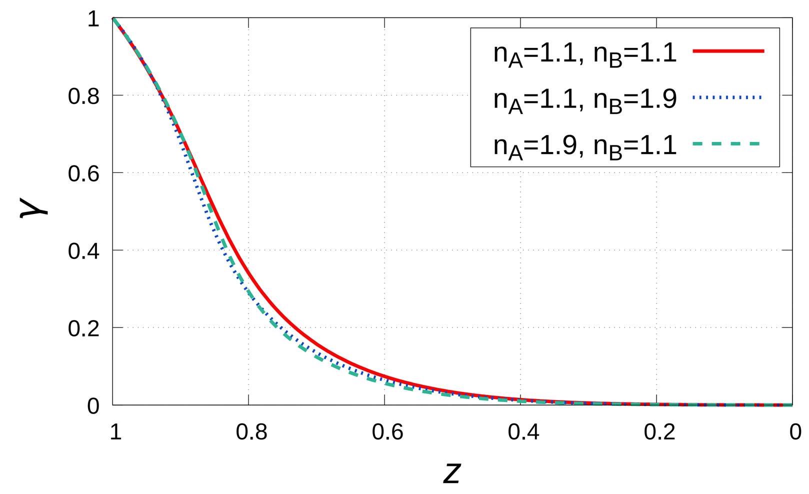

Figure 3. Diffusion profiles of hypothetical binary systems.

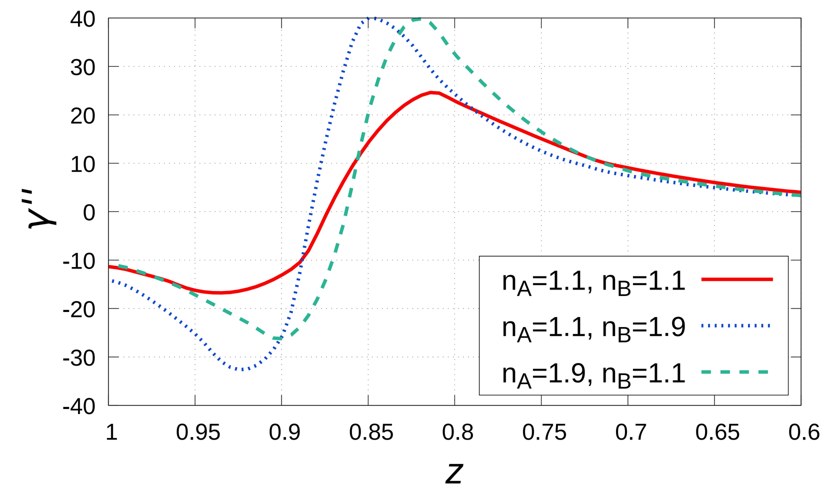

Figure 4. Second derivative of diffusion profiles in Fig. 3.

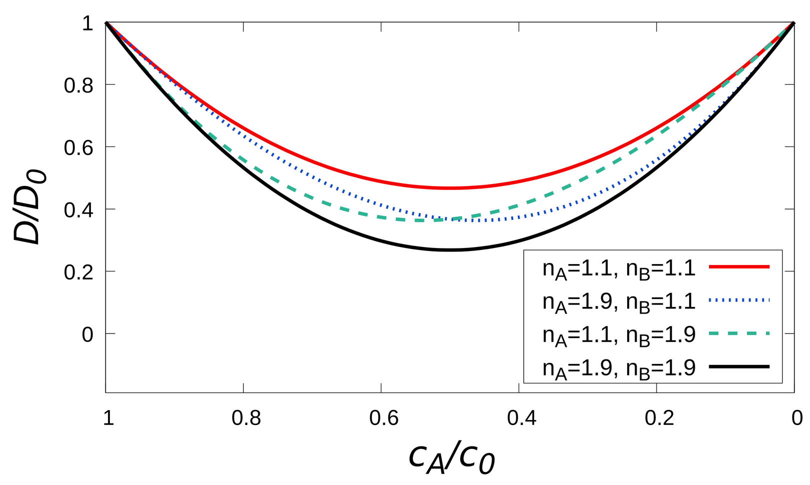

Figure 5. Interdiffusion coefficients of each case expressed in Eq. (2).

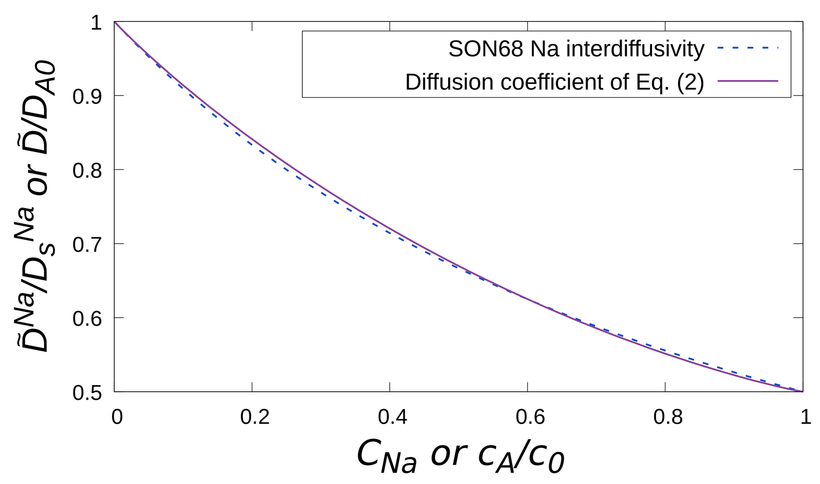

Figure 6. Comparison of diffusion coefficients.

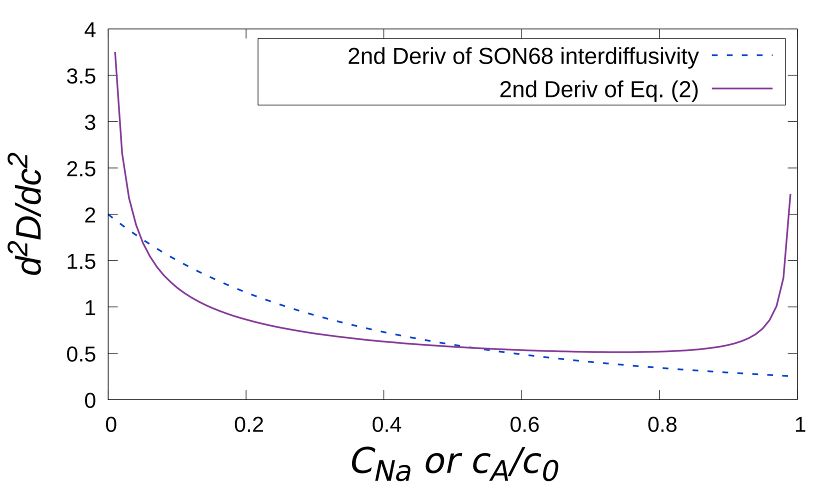

Figure 7. Second derivative of diffusivities in Fig. 6.

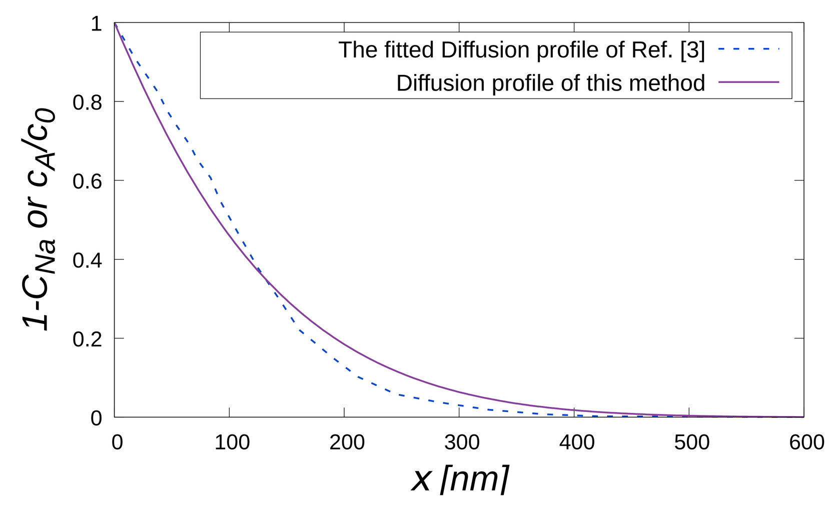

Figure 8. Comparison of diffusion profiles between SON68 Na profile at 90°C for 10 days and the diffusion profile calculated by the present method. Here, $D_s^{Na} = D_{A0}$.

Results - Case 2: a surrogate nuclear waste glass, SON68

In the interdiffusion occurring at Na-ion sites of SON68, a surrogate nuclear waste glass, the interdiffusion coefficient is typically expressed as a function of concentration[3]:

$$\tilde{D}^{Na} = \frac{D_s^{Na} D_b^{Na}}{C_{Na} D_s^{Na} + (1 - C_{Na}) D_b^{Na}} \quad (4)$$

where $D_s^{Na}/D_b^{Na} = 2$. A comparison of these diffusion coefficients and their second derivatives as a function of concentration is presented in Fig. 6 and 7.

Figure 8 presents the Na diffusion profile of SON68 and the concentration-distance plot calculated using the methodology proposed in this work. Despite the discrepancy in the second derivative of the diffusivity, the numerical results obtained from our methodology demonstrate good agreement with the fitted experimental data.

Conclusions

- **Methodology**: We derived the solutions numerically by extending the analytical method proposed in previous studies. We solved the diffusion equation by using the serial transformation, shooting method, and trial-and-error procedure.
- **Key Finding**: The diffusion coefficient, which is a function of the exponents n_A, n_B, determines the curvature of the solution to the diffusion equation. The proposed methodology was applied to characterize the alkali interdiffusion profile in nuclear waste glass.

References

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