Gravity Induced Diffusion: Sedimentation in Condensed Matter

Bartek Wierzba

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In the paper the mathematical model describing the gravity induced sedimentation process in multicomponent system is presented. The model is based on the generalized interdiffusion method (bi-velocity method): (1) the volume continuity equation, (2) equation of motion, (3) Cauchy stress tensor and (4) Nernst Planck flux formulae. The method is applied to simulate the sedimentation processes of the selenium isotopes and the ternary InSbGe system.

Keywords gravity, interdiffusion, pressure, sedimentation, thermodynamics, volume continuity

1. Introduction

The sedimentation process, i.e. gravity induced diffusion, is generally known as the transport phenomena of macroscopic solutes induced by gravitational or centrifugal field.^[1] The sedimentation of isotope atoms in liquids is important from the point of view of separation of isotopes.^[2] Enriched isotopes are crucial in the fields of atomic energy ²³⁵U, ⁶Li, etc.^[3] medical treatment ⁵⁰Cr, ¹⁶⁸Yb, etc.^[4] and in the information technology field for quantum computing ²⁹Si, etc.^[5] In the 1970s, Barr and Smith and Anthony^[6,7] investigated the sedimentation of Au atoms in elemental metals (K, In and Pb) with low melting temperatures under maximum acceleration fields of $1\text{--}2 \times 10^5$ g. In 1996, Mashimo et al. developed an ultracentrifuge apparatus that can generate an acceleration field up to 10^6 g for long times at high temperatures.^[8] The second-generation ultracentrifuge was newly developed, in 2001.^[9] Using this apparatus he studied the sedimentation the substitutional solute atoms in different elements^[10–12] e.g. ultracentrifuge experiments at high temperature on elemental selenium to examine the sedimentation of isotope atoms in liquid matter.^[2]

Almost all sedimentation processes are described by the Lamm equation proposed in 1929.^[13] This classical equation was formulated for axially symmetric macroscopic particles on the basis of macroscopic mechanics and thermodynamics. The fundamental idea of Lamm is that the driving force between the centrifugal field acting on the macro solute is given by the difference between the centrifugal force and the buoyant force caused by the surrounding liquid solvent.^[1] Several approaches to the Lamm equation were made. Brenner and Condiff

extended method for particles of arbitrary shape and considered the rotation effect.^[14] However in these approaches the self-interaction effects among macroscopic solutes caused by the centrifugal field are not considered, therefore, the driving force is not expressed as a function of solute concentration, i.e. the density of the mixture solvent does not change with concentration.^[1]

In 1988 Mashimo proposed an equation for describing the diffusion of atoms induced by the centrifugal field in a two component system.^[1] His theory is based on linear irreversible thermodynamics (Onsager relations) and the Nernst-Einstein relation considering the effect of concentration change.^[1] The Mashimo's theory considers the chemical activity of the simulated system by introducing the Q parameter (the ratios of the diffusion coefficient matrix). The disadvantage of the Mashimo theory is the assumption of the unknown diffusivity under the combined stress and gravity forces.

In the previous paper the bi-velocity method, the rigorous mathematical derivation of the mass, momentum and energy conservations laws and the results of the method for binary Bi-Sb diffusion couple were presented.^[15] In this work the model is applied to simulate the multicomponent sedimentation process when the ideality sweeping statement is applied (i.e. chemical activity is equal to the concentration). Using the bi-velocity method for the first time the application of the formalism in modeling the ternary interdiffusion of selenium isotopes is shown.

2. Mashimo et al.^[16,17] Sedimentation Model

Mashimo model based on the Onsager flux expression, has the form:

$$J_i = - \sum_l \left(D_{il}^1 \frac{\partial c_l}{\partial x} \right) + \sum_j \left(\frac{D_{ij}^2}{RT} g (M_j - M_j^*) \right) c_i, \\ i = 1, 2, \dots, r \quad (\text{Eq 1})$$

where J_i , c_i and M_i denote the overall flux (diffusion and convection), the concentration and atomic mass of i th

Bartek Wierzba, Faculty of Materials Science and Ceramics, Interdisciplinary Centre for Materials Modeling, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Cracow, Poland. Contact e-mail: bwierzba@agh.edu.pl.

component, respectively. M_j^* is the effective mass of the surrounding solvent mixture per molar volume. R , T and g denotes the gas constant, temperature and gravity force, respectively. D_{il}^1 denotes the intrinsic diffusion coefficient, D_{ij}^2 is the unknown (experimentally determined) sedimentation coefficient under the gravity force.

The effective mass of the surrounding solvent mixture per molar volume is expressed by the weighted average:

$$M_j^* = \left(\sum_l \frac{\Omega_l}{\Omega_j} c_l M_l \right) / \left(\sum_l c_l \right), \quad j = 1, 2, \dots, r \quad (\text{Eq 2})$$

where Ω_j denote the partial molar volume of the j th component.

The diffusion coefficients are expressed by the phenomenological transport coefficients, L_{ij} , and chemical potential, μ_j^{ch} :^[16]

$$D_{il}^1 = \sum_l \left(L_{ij} \frac{\partial \mu_j^{\text{ch}}}{\partial c_l} \right), \quad D_{ij}^2 = L_{ij} \frac{kT}{c_i}, \quad i, j = 1, 2, \dots, r \quad (\text{Eq 3})$$

Consequently, using the flux equation Eq 1, Mashimo derived the conservation law in the form of the second Fick's law:

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left(- \sum_l \left(D_{il}^1 \frac{\partial c_l}{\partial x} \right) + \sum_j \left(\frac{D_{ij}^2}{RT} g (M_j - M_j^*) \right) c_i \right), \quad i = 1, \dots, r \quad (\text{Eq 4})$$

It is worth noticing, that in such description of the sedimentation process, the drift (convection) velocity is expressed by:

$$v^{\text{drift}} = \sum_j \left(\frac{D_{ij}^2}{RT} g (M_j - M_j^*) \right). \quad (\text{Eq 5})$$

The presented model was used by Mashimo to simulate the sedimentation of binary systems, mainly the Bi-Sb, Se-Te and In-Pb. In the next section the mathematical model describing the gravity induced sedimentation process in multicomponent system is presented.

3. The Conservation of Momentum and Volume Continuity (Bi-velocity Method)

The overall velocity of the i th component, v_i , is a sum of diffusion, Darken (convection) and deformation velocities, respectively:

$$v_i = v_i^d + v^{\text{drift}} = v_i^d + v^D + v^\sigma \quad (\text{Eq 6})$$

The component diffusion flux, should be expressed by the proper constitutive formula. In this work the Nernst-Planck flux equation^[18,19] is used:

$$J_i^d \equiv \rho_i v_i^d = \rho_i B_i F_i, \quad (\text{Eq 7})$$

where B_i and F_i denote the mobility and the forces acting on the i th component, respectively;

$$F_i = -\text{grad}(\mu_i^{\text{ch}} + \mu_i^m) + F_i^{\text{centr}} = -\text{grad} \mu_i + F_i^{\text{centr}} \quad (\text{Eq 8})$$

where μ_i is the diffusion potential; μ_i^{ch} and μ_i^m denote the chemical and mechanical potentials. F_i^{centr} is the centrifugal force acting on the i th component ($F_i^{\text{centr}} = M_i g$, where M_i is the molar mass of the i th component and g is gravitation force).

The mechanical potential in case of sedimentation processes is expressed as:

$$\mu_i^m = \Omega_i^m p^g \quad (\text{Eq 9})$$

where Ω_i^m denote the partial mass volume of the i th component and p^g is a pressure, Eq 9.

By Newton's law the rate of momentum change equals the overall force acting on the mass in $|\Omega(t)|$:

$$\begin{aligned} \frac{d}{dt} \int_{|\Omega(t)|} \rho v^m dx &= F^{\text{total}} = \sum_i F_i^{\text{total}} \\ &= \sum_i \frac{d}{dt} \int_{|\Omega_i(t)|} \rho_i v_i dx = \sum_i (F_i^\sigma + F_i^{\text{ext}}). \end{aligned} \quad (\text{Eq 10})$$

where the force of elastic stress, F_i^σ is defined:

$$F_i^\sigma = \int_{|\Omega_i(t)|} \text{div}(\Omega_i^m \rho_i \sigma) dx, \quad (\text{Eq 11})$$

where σ denotes Cauchy stress tensor.

In case of the sedimentation process the external force F^{ext} is induced by the buoyant force, thus:

$$F_i^{\text{ext}} = F_i^g = \int_{|\Omega_i(t)|} \rho_i r \omega^2 dx. \quad (\text{Eq 12})$$

Applying the formulae (10)-(12) results in the i -component momentum change in a subregion $|\Omega_i(t)|$:

$$\frac{d}{dt} \int_{|\Omega_i(t)|} \rho_i v_i dx = \int_{|\Omega_i(t)|} \text{div}(\rho_i \Omega_i^m \sigma) dx + \int_{|\Omega_i(t)|} \rho_i r \omega^2 dx \quad (\text{Eq 13})$$

Using the Liouville theorem the left hand side of Eq 13 becomes:

$$\begin{aligned} \frac{d}{dt} \int_{|\Omega_i(t)|} \rho_i v_i dx &= \int_{|\Omega_i(t)|} \left(v_i \left(\frac{\partial \rho_i}{\partial t} + \text{div}(\rho_i v_i) \right) \right. \\ &\quad \left. + \rho_i \left(\frac{\partial v_i}{\partial t} + v_i \cdot \text{grad} v_i \right) \right) dx \\ &= \int_{|\Omega_i(t)|} \rho_i \frac{Dv_i}{Dt} \Big|_{v_i} dx. \end{aligned} \quad (\text{Eq 14})$$

From the arbitrariness of the subregion $|\Omega_i(t)|$ Eq 13 becomes:

$$\rho_i \frac{Dv_i}{Dt} \Big|_{v_i} = \text{div}(\rho_i \Omega_i^m \sigma) + \rho_i r \omega^2 \quad \text{for } i = 1, \dots, r.. \quad (\text{Eq 15})$$

By summing Eq 15 for all components the overall equation of motion in all media in which diffusion is non-negligible is:

$$\sum_i \rho_i \frac{Dv_i}{Dt} \Big|_{v_i} = \text{div} \sigma + \rho r \omega^2. \quad (\text{Eq 16})$$

where r is a radius and ω the angular speed.

To calculate the stationary sedimentation process the mechanical equilibrium should be assumed, thus the above equation of motion is reduced to the following form:

$$0 = \text{div} \sigma + \rho r \omega^2. \quad (\text{Eq 17})$$

3.1 Volume Continuity Eq 15

In linear irreversible thermodynamics the partial molar volumes are intensive parameters and are not conserved. The volume, $|\Omega(t)|$ occupied by the mixture at the moment t , $|\Omega(t)| = \int_{\Omega(t)} dx$, is affected by the distribution of every mixture component and stress field. In this paper the limiting situation, when the volume changes due to the external stress field only (gravity), is analyzed, thus:

$$\int_{|\Omega(t)|} \text{div}(\rho \Omega^m v) dx = \int_{|\Omega(t)|} \text{div} v^\sigma dx. \quad (\text{Eq 18})$$

Integrals can be omitted and differential form of the VCE follows:

$$\text{div}(\rho \Omega^m v) = \text{div} v^\sigma, \quad (\text{Eq 19})$$

3.2 Cauchy Stress Tensor

A common approach when defining the relation between pressure and energy of the stress field in solids is to neglect the torsion.^[20] Here, in order to consider the overall stress energy, Schur decomposition^[21] is used. Such transformation allow to diagonalize the symmetric stress tensor. The pressure (generated by the external force) is defined than as the trace of the diagonal stress tensor (diagonalized Cauchy stress tensor, σ),^[22]

$$p^g = -\frac{1}{3} \text{tr}(\sigma^*) = -\frac{1}{3} \sigma^* : \mathbf{I} = -\frac{1}{3} (\lambda_1 + \lambda_2 + \lambda_3), \quad (\text{Eq 20})$$

where λ_i are the eigenvalues of Cauchy stress tensor.

Finally the stress tensor will be defined from the definition of the pressure,

$$\sigma = -p^g \mathbf{I} \Rightarrow \text{div} \sigma = -\text{div}(p^g \mathbf{I}) = -\text{grad} p^g. \quad (\text{Eq 21})$$

The momentum conservation law, Eq 17, has now the form

$$\text{grad} p^g = \rho r \omega^2, \quad (\text{Eq 22})$$

where the stress tensor and pressure are related by Eq 20 and 21.

3.3 Initial Conditions

The initial density distribution of the i th component: ρ_i^0 .

3.4 Boundary Conditions

The diffusion flux of the i th component at the mixture boundary, $\rho_i v_i^d(t) \cdot n = 0$ on $\partial|\Omega|$, where n represents the unit vector normal to the boundary i.e., in the closed system analyzed here, the mass flow through the mixture boundaries does not occur.

3.5 Numerical Solution

The solution of the presented model was obtained in several steps: (1) discretization of the problem (mathematical reformulation), (2) numerical solution using Finite Difference Method (FDM), (3) solving the resulting system of ordinary differential equations and computer implementation of method. The differential equations solver based on the Runge-Kutta-Fehlberg method with adaptive stepsize control. Fehlberg discovered a fifth-order method with six function evaluations where another combination of this six functions gives a fourth-order method. The difference between these two estimates can then be used as an estimate of the truncation error to adjust the stepsize.^[23]

The schematic presentation of the two dimensional model is shown on Fig. 1. The simulations consider the diffusion flux along the gravity direction. The dotted line represent the one-dimensional mapping of the simulated results. The forces acting on the surface of the sample in X, Y Cartesian coordinate system are defined as:

$$\begin{aligned} F_x &= \omega x, \\ F_y &= 0. \end{aligned}$$

Using such representation the equations describing the forces in the rotated system ($X'Y'$) are:

$$\begin{aligned} F_{x'} &= \omega^2 ((\ell + y') \sin \alpha + x' \cos \alpha) \cos \alpha, \\ F_{y'} &= \omega^2 ((\ell + y') \sin \alpha + x' \cos \alpha) \sin \alpha. \end{aligned}$$

4. Results

As an example the sedimentation process in the Se-Te binary system^[24] is presented. The results of the simulations are compared with the Mashimo et al. experiments and his calculations. The data used to calculate the sedimentation process in Se-Te system are presented in Table 1. The

Fig. 1 The schematic presentation of the 2 dimensional sedimentation model

Table 1 The data used to simulate the sedimentation process in Se-Te binary systems

Component	Atomic mass (M_i), g/mol	Molar volume (Ω_i), cm ³ /mol	Initial composition, at. %
SeTe system, $T = 533$ K, angular speed 143,000 rev/min			
Se	78.96	17.99	70
Te	127.6	20.45	30

Fig. 2 The sedimentation process in Se-Te system

presented simulation results were calculated using the steady state approximation, i.e. the simulations were performed until no change of the concentration profile was observed.

Table 2 The data used to simulate the sedimentation process for composition ratio of ⁸²Se/⁷⁶Se

Component	Atomic mass (M_i), g/mol	Molar volume (Ω_i), cm ³ /mol	Initial composition, at. %
$T = 573$ K, angular speed 145,000 rev/min			
⁸² Se	82	16.45	9.2
⁷⁶ Se	76	16.45	9.0
Se	78.96	16.45	81.8

Fig. 3 The sedimentation process of Selenium isotopes. The composition ratio of ⁸²Se/⁷⁶Se (line) compared with the experimental results (dots)

Fig. 4 The sedimentation in three-component system In-Ge-Sb

To calculate the sedimentation the two dimensional model was used. The results are shown in Fig. 2. The dots shows the experimental values of the sedimentation process, the dashed line present the simulations from the Mashimo et al.^[24] model and the solid line model presented in this work.

Table 3 The data used to simulate the sedimentation process of InGeSb ternary system

Component	Atomic mass (M_i), g/mol	Molar volume (Ω_i), cm ³ /mol	Initial composition, at. %
$T = 527$ K, angular speed 192,000 rev/min			
In	114.818	15.71	30
Sb	121.769	18.18	30
Ge	72.64	13.65	40

The next example shows the sedimentation of Selenium isotopes. The calculated composition ratio of $^{82}\text{Se}/^{76}\text{Se}$ is compared with the experimental results.^[25] The simulations were performed in three-components system. The two components were the isotopes and the third was the reference ideal component. The data used in calculations is shown in Table 2.

The results of the composition ratio of $^{82}\text{Se}/^{76}\text{Se}$ compared with the (a) experimental results and (b) Mashimo model^[2] are shown in Fig. 3.

The last example, Fig. 4, present the sedimentation in three-component system InGeSb, the Te-free recording material for high speed recording application.^[26] The data used in simulations is shown in Table 3.

5. Conclusions

In this paper a mathematical model describing the gravity induced sedimentation process in multicomponent system is presented. The model is based on the generalized interdiffusion method (bi-velocity method): (1) the volume continuity equation, (2) equation of motion, (3) Cauchy stress tensor and (4) Nernst Planck flux formulae. In the present approach the plastic deformation is neglected. The method was applied to simulate the sedimentation processes of the selenium isotopes and the ternary InSbGe system.

The model can be extended by introducing the elastic stress field induced by the diffusion process. Consequently, the pressure field will consist two parts: (1) the pressure generated by the external field (gravity), p^g and (2) pressure generated by the differences in composition (chemical forces), p^d . The p^d can be calculated from overall dilatation of the system:^[27]

$$\frac{\partial p^d}{\partial t} = -\frac{E}{3(1-2\nu)} \text{div} v^d$$

where: E denote the Young modulus and ν Poisson number. In such a case the diffusion velocity can be rewritten as:

$$v_i^d = -B_i \text{grad}(\mu_i^{ch} + \Omega_i p^g + \Omega_i p^d) + B_i M_i r \omega^2.$$

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References

1. T. Mashimo, Self-Consistent Approach to the Diffusion Induced by a Centrifugal Field in Condensed Matter; Sedimentation, *Phys. Rev. A*, 1988, **38**, p 4149
2. T. Mashimo et al., Sedimentation of Isotope Atoms in Monatomic Liquid Se, *Appl. Phys. Lett.*, 2007, **91**, p 231917
3. S. Villani, *Isotope Separation*, American Nuclear Society, Hinsdale, 1976
4. G. Friedlander, J.W. Kennedy, E.S. Macias, and J.M. Millar, *Nuclear and Radiochemistry*, 3rd ed., Wiley, New York, 1981
5. M.N. Leuenberger and D. Loss, Quantum Computing in Molecular Magnets, *Nature (London)*, 2001, **410**, p 789
6. L.W. Barr and F.A. Smith, Observations on the Equilibrium Distribution of Gold Diffusing in Solid Potassium in a Centrifugal Field, *Phil. Mag.*, 1969, **20**, p 1293
7. T.R. Anthony, Sedimentation in the Solid State, *Acta Metall.*, 1970, **18**, p 877
8. T. Mashimo, S. Okazaki, and S. Shibasaki, Ultracentrifuge Apparatus to Generate a Strong Acceleration Field of Over 1 000 000 g at a High Temperature in Condensed Matter, *Rev. Scient. Instrum.*, 1996, **67**, p 3170
9. T. Mashimo, X.S. Huang, T. Osakabe, M. Ono, M. Nishihara, H. Ihara, M. Sueyoshi, K. Shibasaki, S. Shibasaki, and N. Mori, Advanced High-Temperature Ultracentrifuge Apparatus for Mega-Gravity Materials Science, *Rev. Sci. Instr.*, 2003, **74**, p 160
10. T. Mashimo, S. Okazaki, and S. Tashiro, Sedimentation of Atoms in Solid under a Strong Acceleration Field of around 1 Million g, *Jpn. J. Appl. Phys.*, 1997, **36**, p L498
11. T. Mashimo, T. Ikeda, and I. Minato, Atomic-scale Graded Structure Formed by Sedimentation of Substitutional Atoms in a Bi-Sb Alloy, *J. Appl. Phys.*, 2001, **90**, p 741
12. T. Mashimo, M. Ono, T. Kinoshita, X.S. Huang, T. Osakabe, and H. Yasuoka, Sedimentation Process for Atoms in Bi-Sb System Alloy under a Strong Gravitational Field: A New Type of Diffusion of Substitutional Solutes, *Philos. Mag. A*, 2002, **82**, p 591
13. O. Lamm, Die Differentialgleichung der Ultrazentrifugierung, *Ark. Mat. Astron. Fys.*, 1929, **21B**, p 1
14. H. Brenner and D.W. Condiff, Transport Mechanics in Systems of Orientable Particles III. Arbitrary Particles, *J. Colloid Int. Sci.*, 1972, **41**, p 228
15. B. Wierzbna and M. Danielewski, Segregation in Multicomponent Mixtures under Gravity: The Bi-velocity Method, *Phys. A*, 2011, **390**, p 2325
16. T. Mashimo, Self-Consistent Approach to the Diffusion Induced by a Centrifugal Field in Condensed Matter, *Phys. Rev. A*, 1988, **28**, p 4149
17. T. Mashimo, Sedimentation of Atoms in Condensed Matter: Theory, *Phil. Mag.*, 1994, **A70**, p 739
18. W. Nernst, Die elektromotorische Wirkamkeit der Ionen, *Z. Phys. Chem. (N F)*, 1889, **4**, p 129
19. M. Planck, Ber die potentialdierenz zwischen zwei verdnnten lsungen binrer elektrolyte, *Annu. Rev. Phys. Chem.*, 1890, **40**, p 561

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20. R.W. Balluffi, S.M. Allen, W.C. Carter, and R.A. Kemper, *Kinetics of Materials*, Wiley, Hoboken, 2005
21. A. Quarteroni, R. Sacco, and F. Saleri, *Numerical Mathematics*, Springer, New York, 2000
22. M. Danielewski and B. Wierzba, Thermodynamically Consistent Bi-velocity Mass Transport Phenomenology, *Acta Mater.*, 2010, **58**, p 6717
23. W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, *Numerical Recipes in C: The Art of Scientific Computing*. Cambridge University Press, Cambridge, 1992
24. X. Huang, M. Ono, H. Ueno, Y. Iguchi, T. Tomita, S. Okayasu, and T. Mashimo, Formation of Atomic-scale Graded Structure in Se-Te Semiconductor under Strong Gravitational Field, *J. Appl. Phys.*, 2007, **101**, p 113502
25. T. Mashimo, M. Ono, X. Huang, Y. Iguchi, S. Okayasu, K. Kobayashi, and E. Nakamura, Gravity-Induced Diffusion of Isotope Atoms in Monoatomic Solid Se, *EPL*, 2008, **81**, p 56002
26. L. van Pieterson, M. van Schijndel, and J.C.N. Rijpers, Te-free, Sb-based Phase-Change Materials for High-Speed Rewritable Optical Recording, *Appl. Phys. Lett.*, 2003, **83**, p 1373
27. B. Wierzba and M. Danielewski, Entropy Production During Interdiffusion under Internal Stress, *Philos. Mag.*, 2011, **91**, p 3228