*Multi*DiFlux©

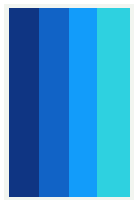
Analysis of Concentration Profiles of Multi-component Diffusion couples

for

Interdiffusion Fluxes and Interdiffusion Coefficients

And

Diffusion Paths



Quantum Semiconductor Algorithms

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Analysis*

•**Concentration profiles** that develop in a solid-solid, ternary diffusion couple can be **analyzed directly for ternary interdiffusion coefficients** defined as average values over selected regions in the diffusion zone.

•These coefficients are calculated from an **integration of interdiffusion fluxes** which are calculated directly from experimental concentration profiles.

*** M. A. Dayananda and Y. H. Sohn, *Metall. Mater. Trans. A.*, 30A (1999) pp. 535-543.**

Determination of Interdiffusion Fluxes*

The interdiffusion fluxes of all components can be evaluated directly from the concentration profiles of a solid-solid diffusion couple at any section x in an n-component system **without** the need for interdiffusion coefficients.

$$\tilde{J}_i(x) = \frac{1}{2t}\int_{C_i(\pm\infty)}^{C_i(x)} (x - x_o)\, dC_i \qquad (i = 1, 2, \ldots, n)$$

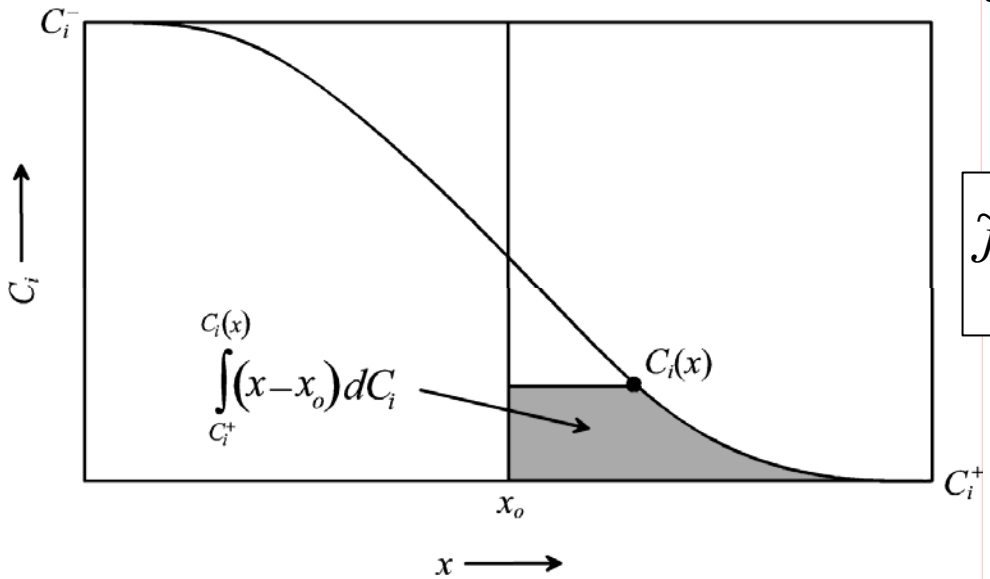
*** M. A. Dayananda and C. W. Kim, *Metall. Trans.*, 10A (1979) 1333.**

Interdiffusion Flux

Calculation from Experimental Concentration Profiles[1,2]

Generalized Fick's Law[3,4]:

$$\tilde{J}_i = -\sum_{j=1}^{n-1} \tilde{D}_{ij}^{n} \frac{\partial C_j}{\partial x} \quad (i = 1, 2, \ldots, n-1)$$



$$\tilde{J}_i(x) = \frac{1}{2t} \int_{C_i^+ \text{ or } C_i^-}^{C_i(x)} (x - x_o)\, dC_i \quad (i = 1, 2, \ldots, n)$$

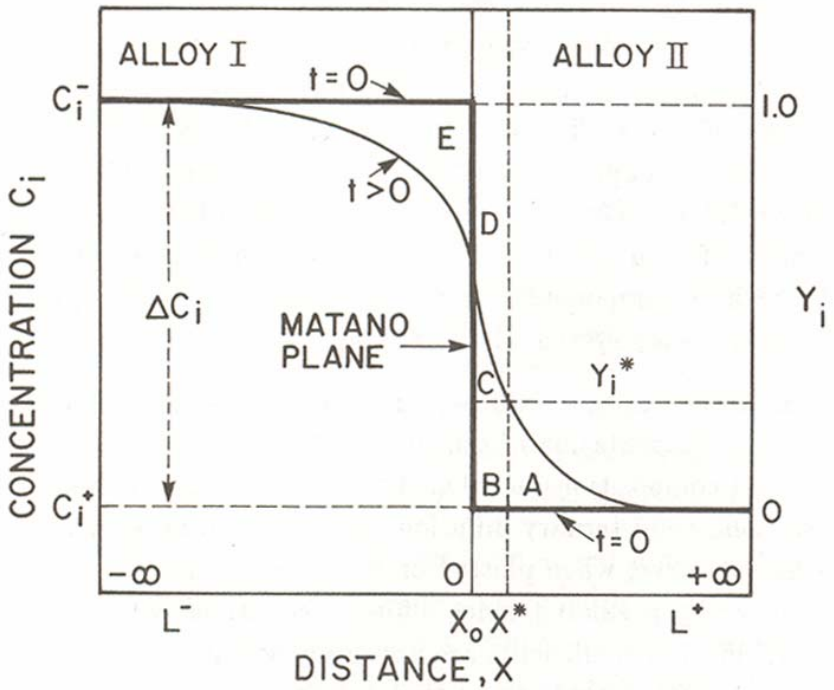
[1] M.A. Dayananda and C.W. Kim, *Metall. Trans. A*, **10A** 1333-1339 (1979).

[2] M.A. Dayananda, *Metall. Trans. A*, **14A** 1851-1858 (1983).

[3] L. Onsager, *Phys. Rev.*, **37** 405-426 (1931).

[4] L. Onsager, *Phys. Rev.*, **38** 2265-2279 (1931).

Flux equations to include molar volume changes



$$Y_i = (C_i - C_i^+) / (C_i^- - C_i^+)$$

$$E+D-A=B+C+D$$

$$=(x^* - x_o)$$

$$J_i^M(x^*) = \frac{\Delta C_i}{2t}\left[Y_i^* \int_{-\infty}^{x^*} \frac{(1-Y_i)}{V_m} dx + (1-Y_i^*) \int_{x^*}^{\infty} \frac{Y_i}{V_m} dx \right] \quad (i = 1,2....n)$$

Integration of Interdiffusion Fluxes

On the basis of Onsager's formalism,

$$\tilde{J}_i = -\tilde{D}_{i1}^3 \frac{\partial C_1}{\partial x} - \tilde{D}_{i2}^3 \frac{\partial C_2}{\partial x} \qquad (i = 1, 2)$$

$$\int_{x_1}^{x_2} \tilde{J}_i dx = -\int_{C_1(x_1)}^{C_1(x_2)} \tilde{D}_{i1}^3 dC_1 - \int_{C_2(x_1)}^{C_2(x_2)} \tilde{D}_{i2}^3 dC_2 \qquad (i = 1, 2)$$

$$= \bar{\tilde{D}}_{i1}^3 \left[C_1(x_1) - C_1(x_2)\right] + \bar{\tilde{D}}_{i2}^3 \left[C_2(x_1) - C_2(x_2)\right] \qquad (i = 1, 2)$$

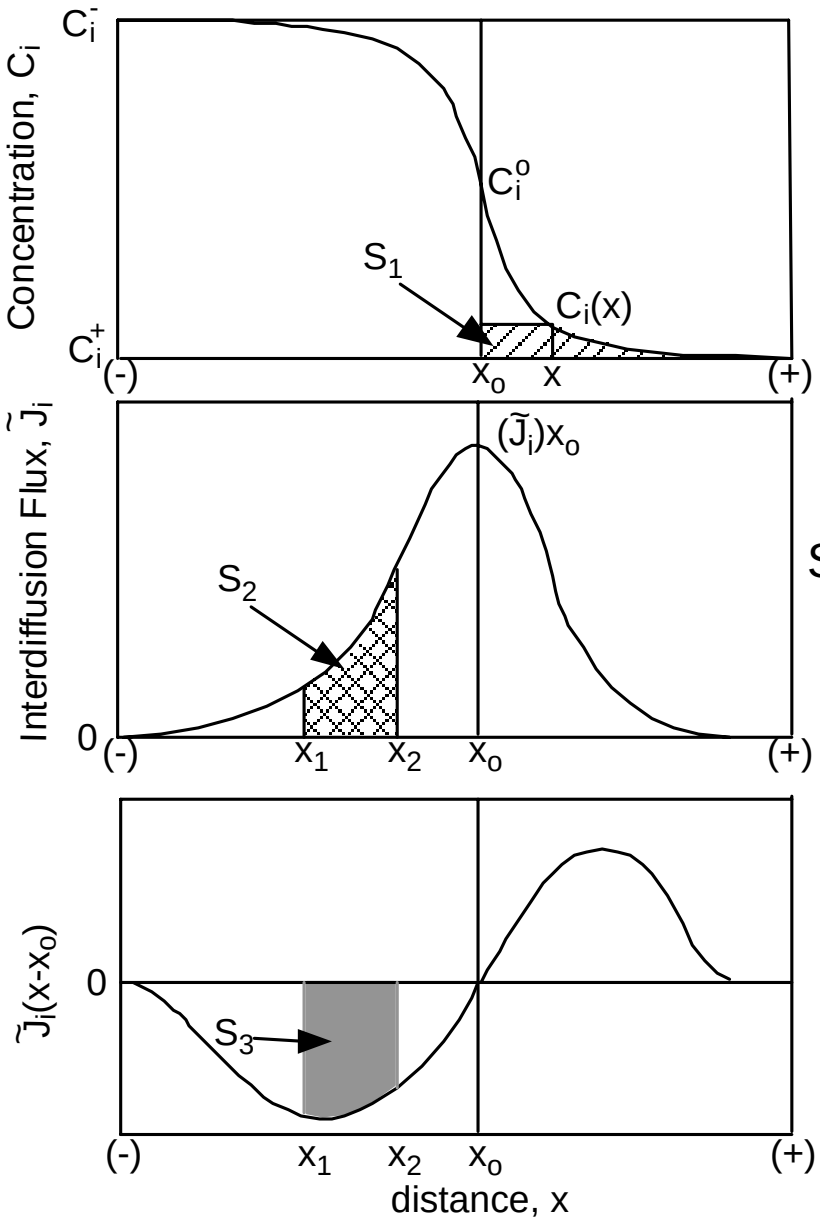
$\bar{\tilde{D}}_{i1}^3$ **and** $\bar{\tilde{D}}_{i2}^3$ **are the average values of main and cross interdiffusion coefficients.**

Multiplying both sides by $(x-x_o)$ and integrating over a selected region, x_1 to x_2 :

$$\int_{x_1}^{x_2} \tilde{J}_i(x-x_o)dx = -\overline{\tilde{D}}_{i1}^{3} \int_{C_1(x_1)}^{C_1(x_2)} (x-x_o)dC_1 - \overline{\tilde{D}}_{i2}^{3} \int_{C_2(x_1)}^{C_2(x_2)} (x-x_o)dC_2 \qquad (i=1,2)$$

$$\int_{x_1}^{x_2} \tilde{J}_i(x-x_o)dx = 2t\left\{\overline{\tilde{D}}_{i1}^{3}\left[\tilde{J}_1(x_1)-\tilde{J}_1(x_2)\right] + \overline{\tilde{D}}_{i2}^{3}\left[\tilde{J}_2(x_1)-\tilde{J}_2(x_2)\right]\right\} \qquad (i=1,2)$$

Determination of $\overline{\tilde{D}}_{ij}^{3}$ (i, j = 1,2) Coefficients



$$S_1 = \int_{C_i^+}^{C_i(x)} (x - x_o)\, dC_i;\quad S_2 = \int_{x_1}^{x_2} \tilde{J}_i\, dx;\quad S_3 = \int_{x_1}^{x_2} \tilde{J}_i (x - x_o)\, dx$$

$$\overline{\tilde{D}}_{ij}^{3} = \int_{C_j(x_1)}^{C_j(x_2)} \tilde{D}_{ij}^{3}\, dC_j \Big/ \int_{C_j(x_1)}^{C_j(x_2)} dC_j \qquad (i = 1,2)$$

Multi*D*iflux Program

DATA_INPUT FILE

Number of Components: 2 or more

Single Phase or Multiphase: 0 or 1 (switch)

Index of Dependent Concentration: 3 for ternary

Data file: C_i vs. x

Diffusion time: t

Number of Interpolation elements for smoothening the experimental data with Hermite polynomials : Variable

Number of diffusion zones: Number of phase layers

Diffusion regions into which each zone is divided for the calculation of interdiffusion coefficients: Variable

Main Output Files

Expt_.out – C_i **vs. x plots**

Conc_interp.out – Interpolated profiles

Flux.out - J_i **vs. x plots (calculated)**

Conc_deriv.out- C_i **Derivatives of**

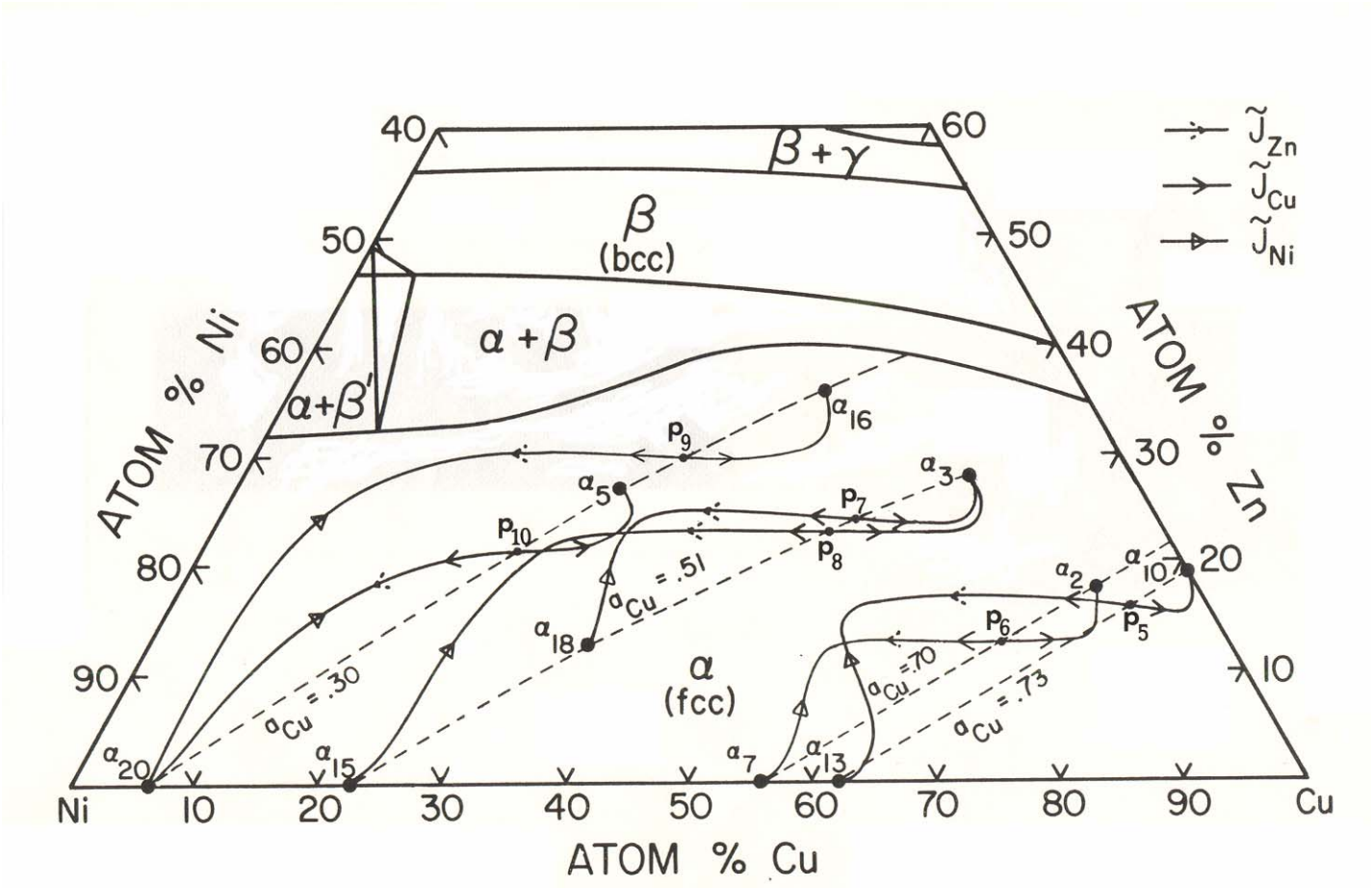
Deriv_nodes_data.out: C_i **Derivatives of at both ends of each interpolation region**

Diff.out - D_{ij} **coefficients (calculated)**

Matano0.out – Locations of Matano plane

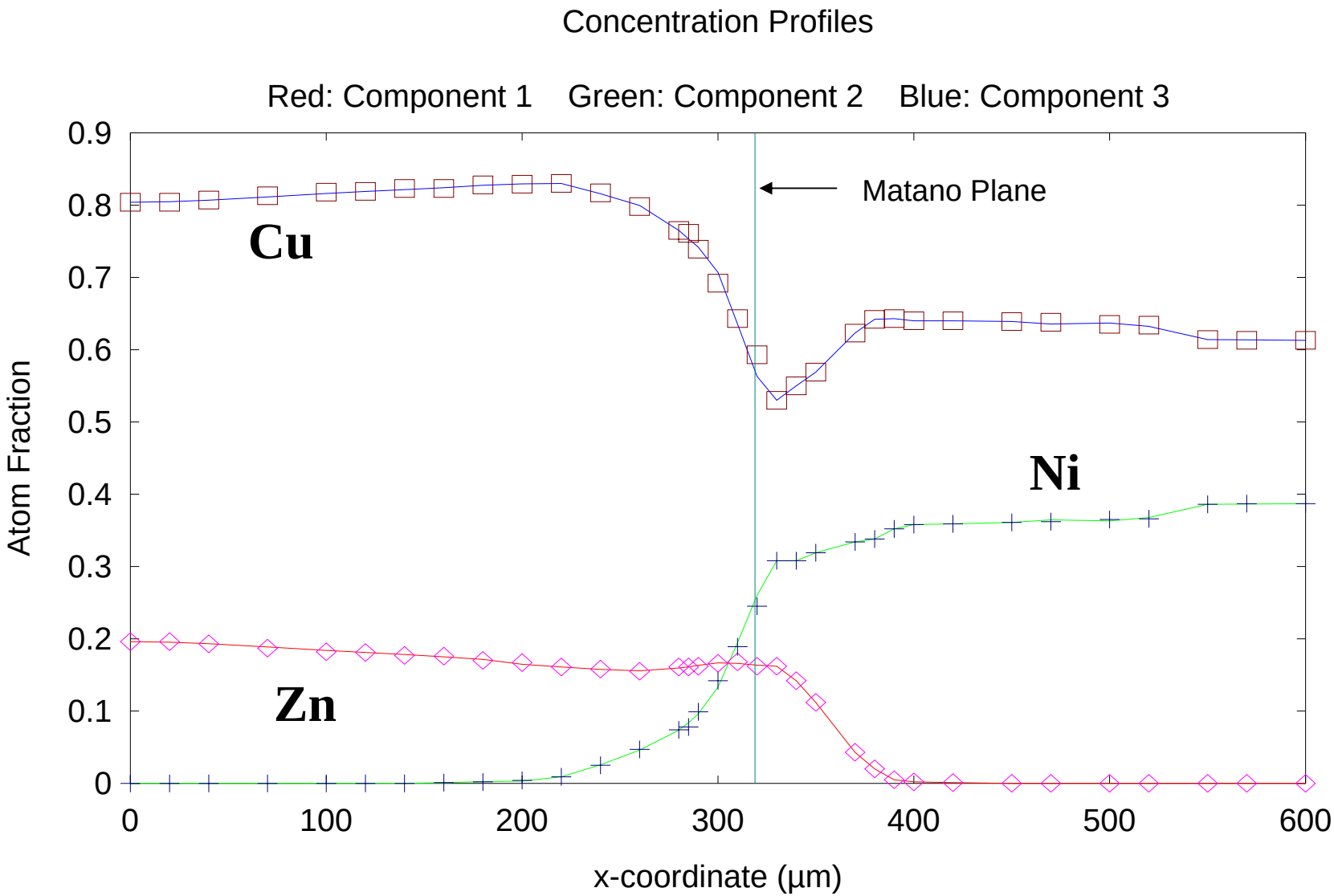
These files are displayed through Gnuplot.

Cu-Isoactivity Couples in the Cu-Ni-Zn System

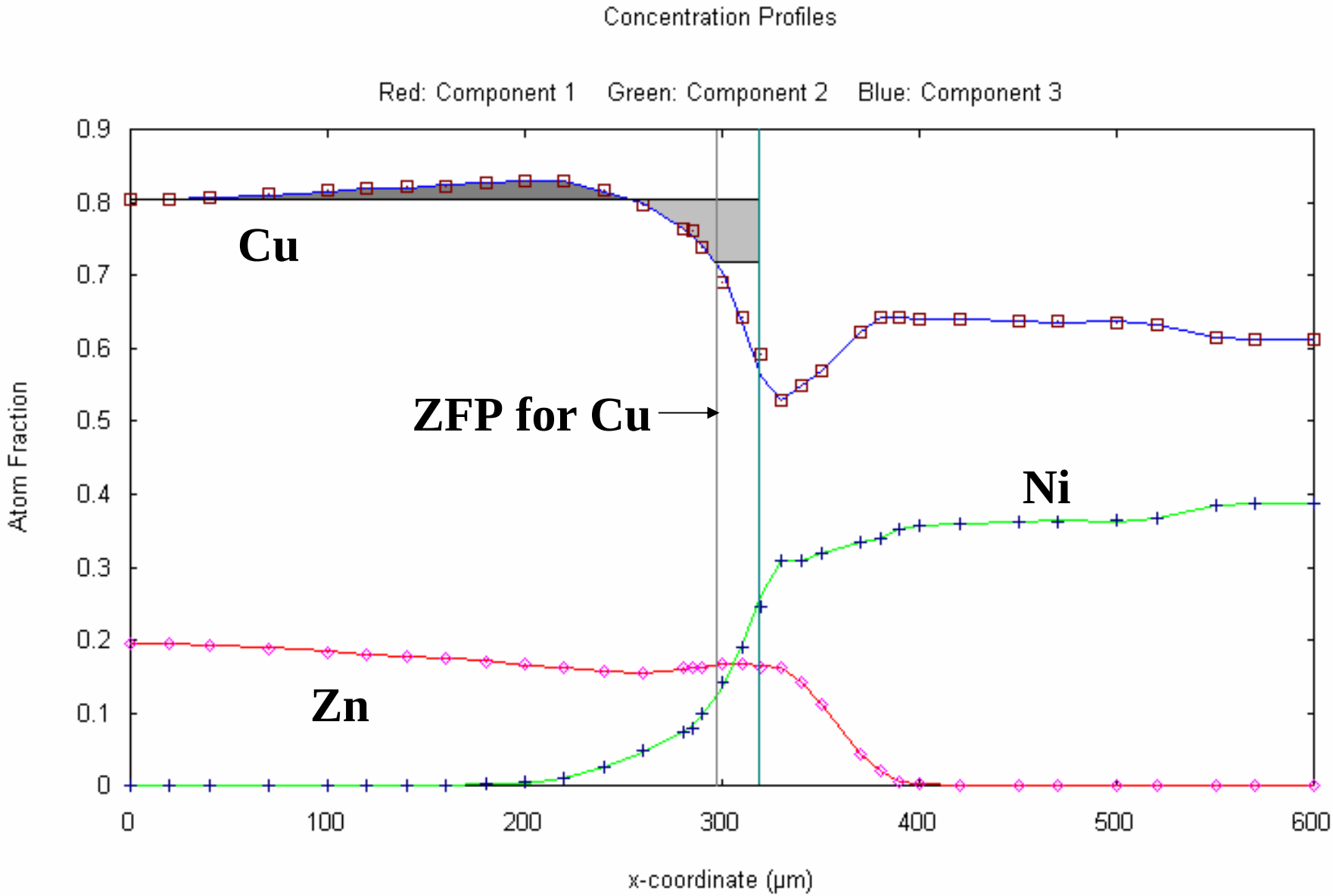


C.W. Kim and M.A. Dayananda, Metall. Trans. A, 15A, (1984) pp. 649-657

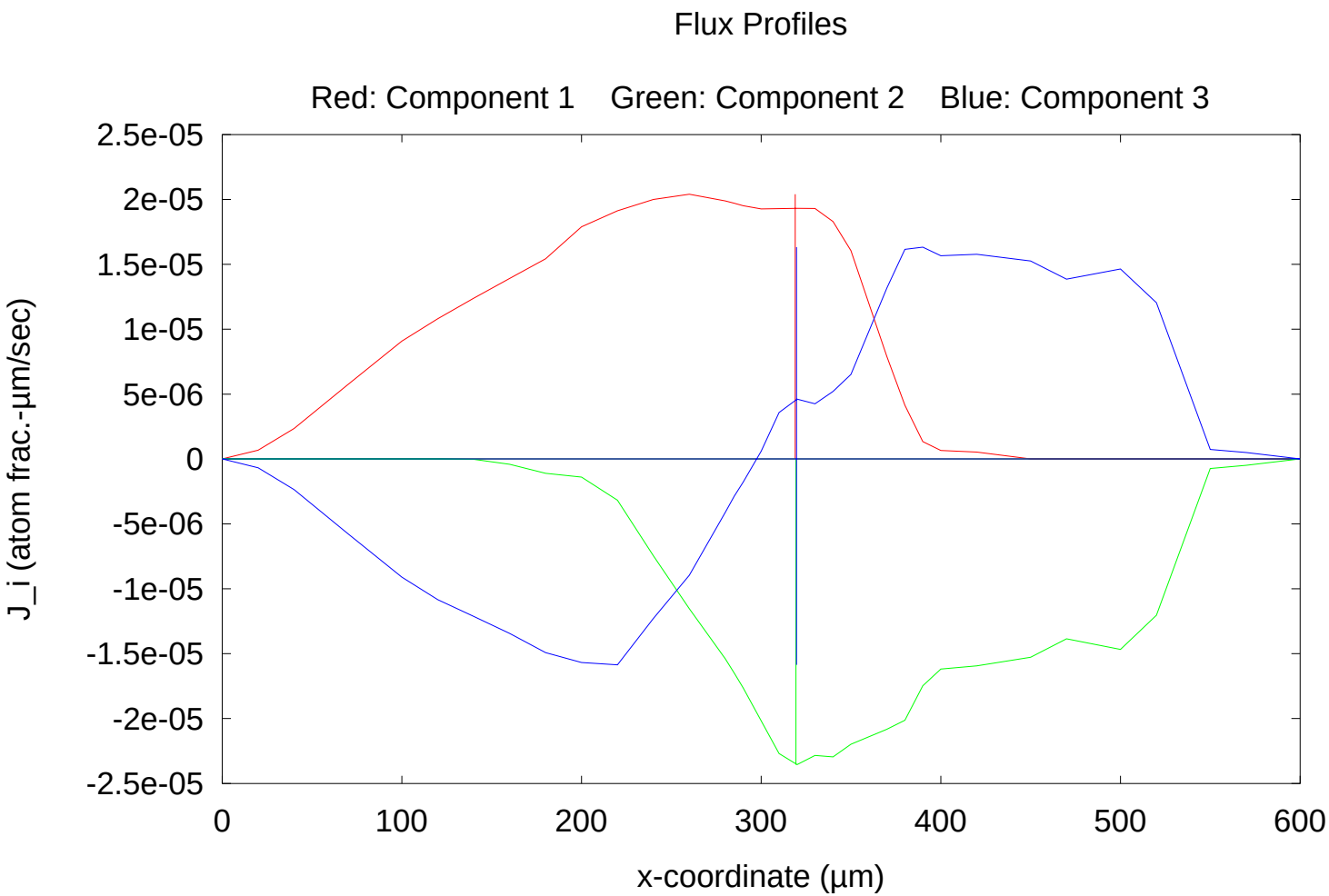
Cu-Isoactivity Cu-Ni-Zn Couple, a_{10} vs a_{13}



Cu-Isoactivity Cu-Ni-Zn Couple, a_{10} vs a_{13}



Flux Profiles for the Couple, a_{10} vs a_{13}



#==

This file shows the diffusion coefficients D_ij

for each element within each zone of the diffusion domain.

#==

Zone1

Element1 xbegin = +0.0000e+000 xend = +3.2000e+002

Dmatrix(2, 2):

+4.8120e-014 -9.5250e-015
-2.8061e-015 +5.3131e-015

#==

Zone2

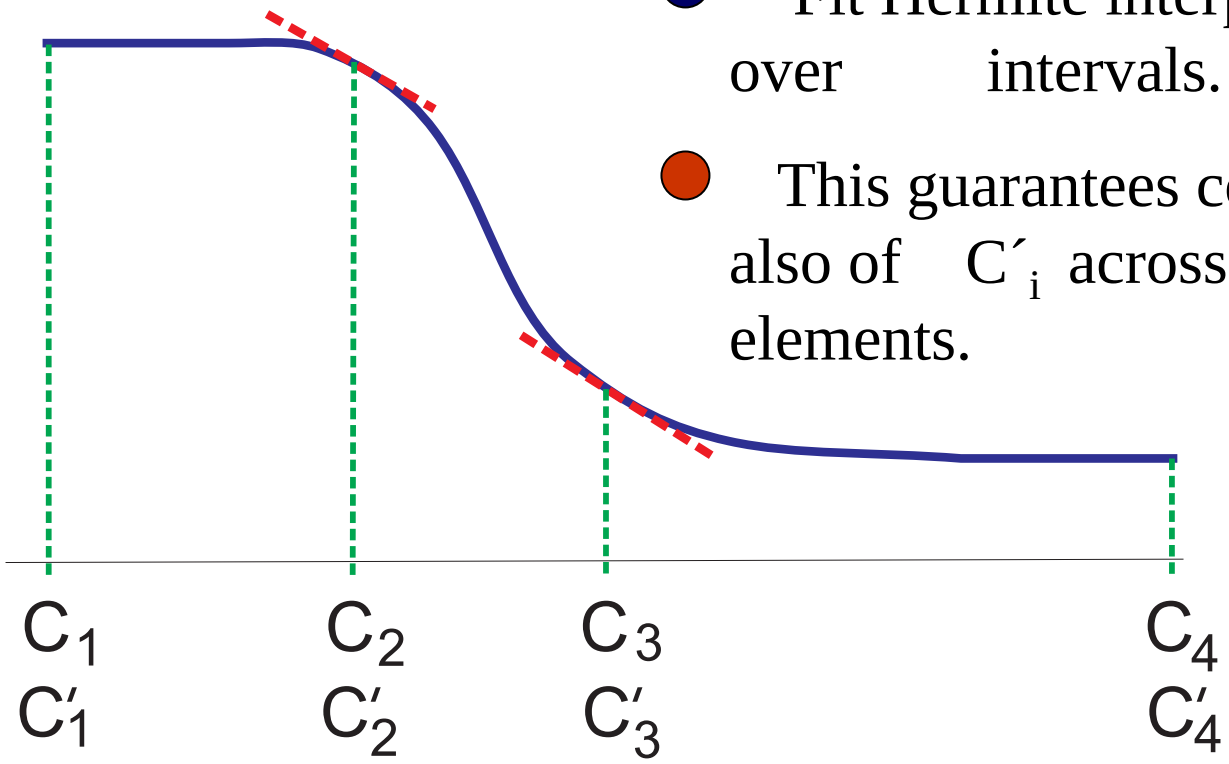
Element1 xbegin = +3.2000e+002 xend = +6.0000e+002

Dmatrix(2, 2):

+6.6662e-015 +1.2323e-015
-8.2553e-015 +1.7341e-014

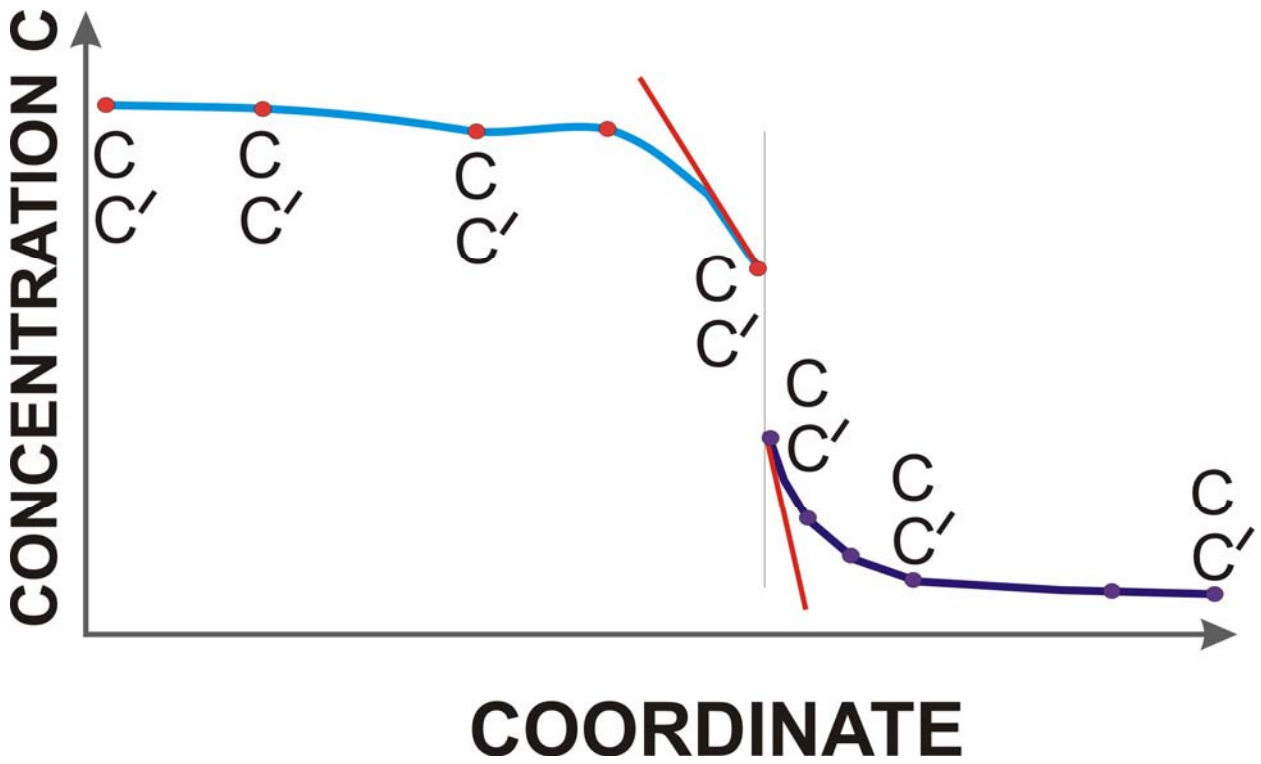
Interpolation of Data

- In the experimental data, C_i are given. We have $C'_i = 0$ at end points.
- Fit Hermite interpolation polynomials over intervals.
- This guarantees continuity of C_i and also of C'_i across interpolation elements.



Hermite Interpolation

Multiphase Diffusion and Interpolation



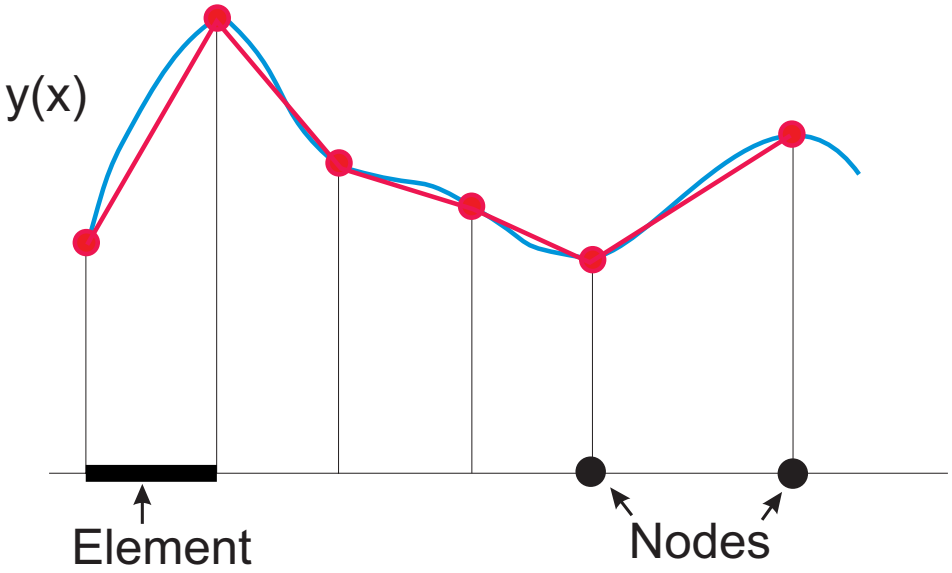
- Create several diffusion zones and interpolate separately.

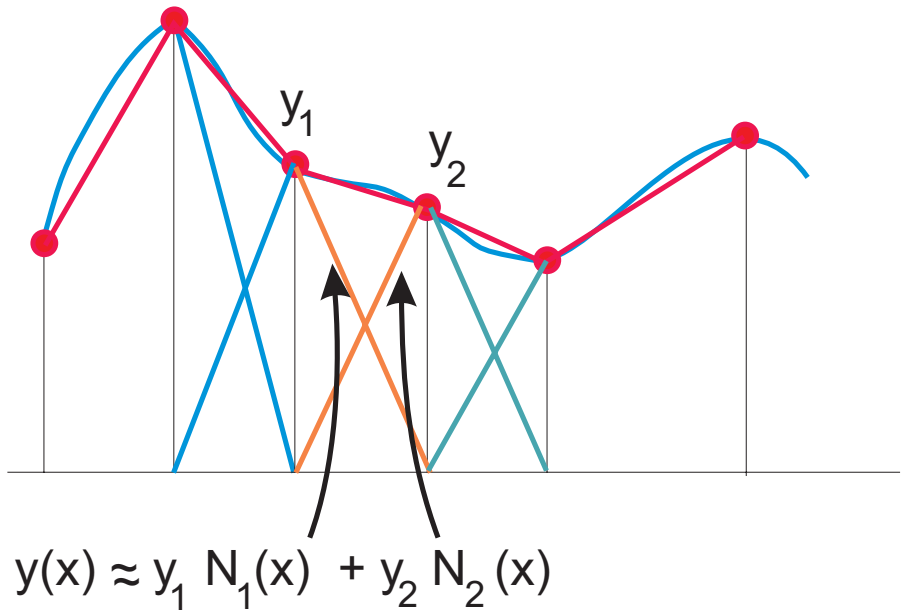
Method of Finite Elements

- Set up an ***action integral**** for the differential equation under study. Break up the physical region into finite elements. The "PHYSICS" is the same in the elements as in the global system.
- Express the physical "field" in terms of unknown nodal values and interpolation polynomials.
- Integrate out the spatial dependence and use a ("nodal") variational method (Principle of Least Action) for determining the nodal variables.
- Derive the system of linear equations representing the original differential equation, and apply boundary conditions.
- Solve the linear equations and obtain nodal values. Reconstruct the full solution using the **same** interpolation functions as before.

*Use Galerkin's method if no action principle exists.

Finite Element Representation of a Function





$$N_1(x) = 1 - x \; ; \quad N_2(x) = x$$

Example: Linear Elements

Diffusion Equation

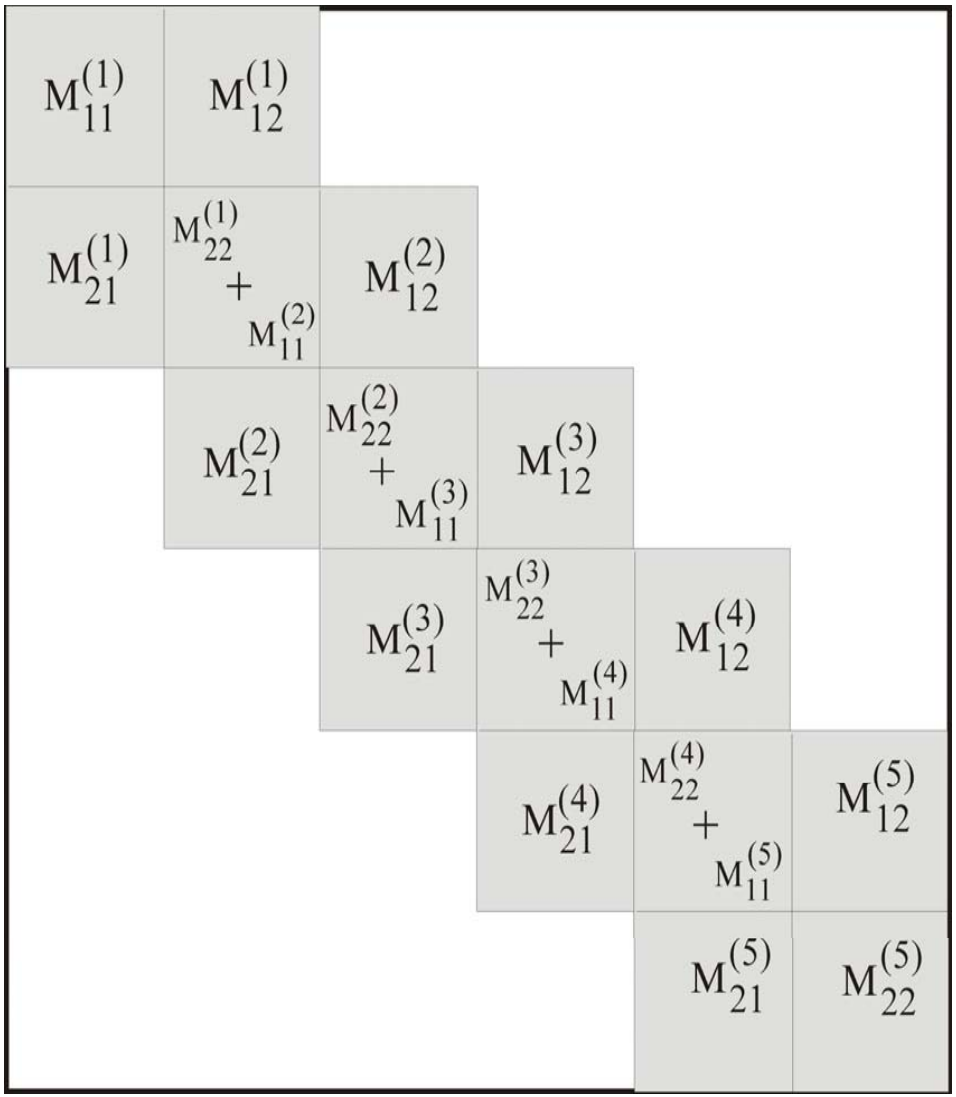
$$\frac{\lambda}{2}\frac{dC_i}{d\lambda}+\frac{d}{d\lambda}\left(D_{ij}\left(\{C_k\}\right)\frac{dC_j}{d\lambda}\right)=0;\quad \lambda=x/\sqrt{t}.$$

For FEA using Galerkin's method, project the equation along test functions or shape functions. Express C_i in terms of shape functions and unknown nodal values $C_{i\alpha}$ for C_i and integrate out the coordinate dependence.

This leads to simultaneous equations for the nodal values of $C_{i\alpha}$

$$\int d\lambda\left(N_\alpha\frac{\lambda}{2}\frac{dN_\beta}{d\lambda}\right)C_{\beta i}+\int d\lambda\left(\frac{dN_\alpha}{d\lambda}D_{ij}\frac{dN_\beta}{d\lambda}\right)C_{\beta j}=0.$$

Concentration Continuity using Finite Element Overlay

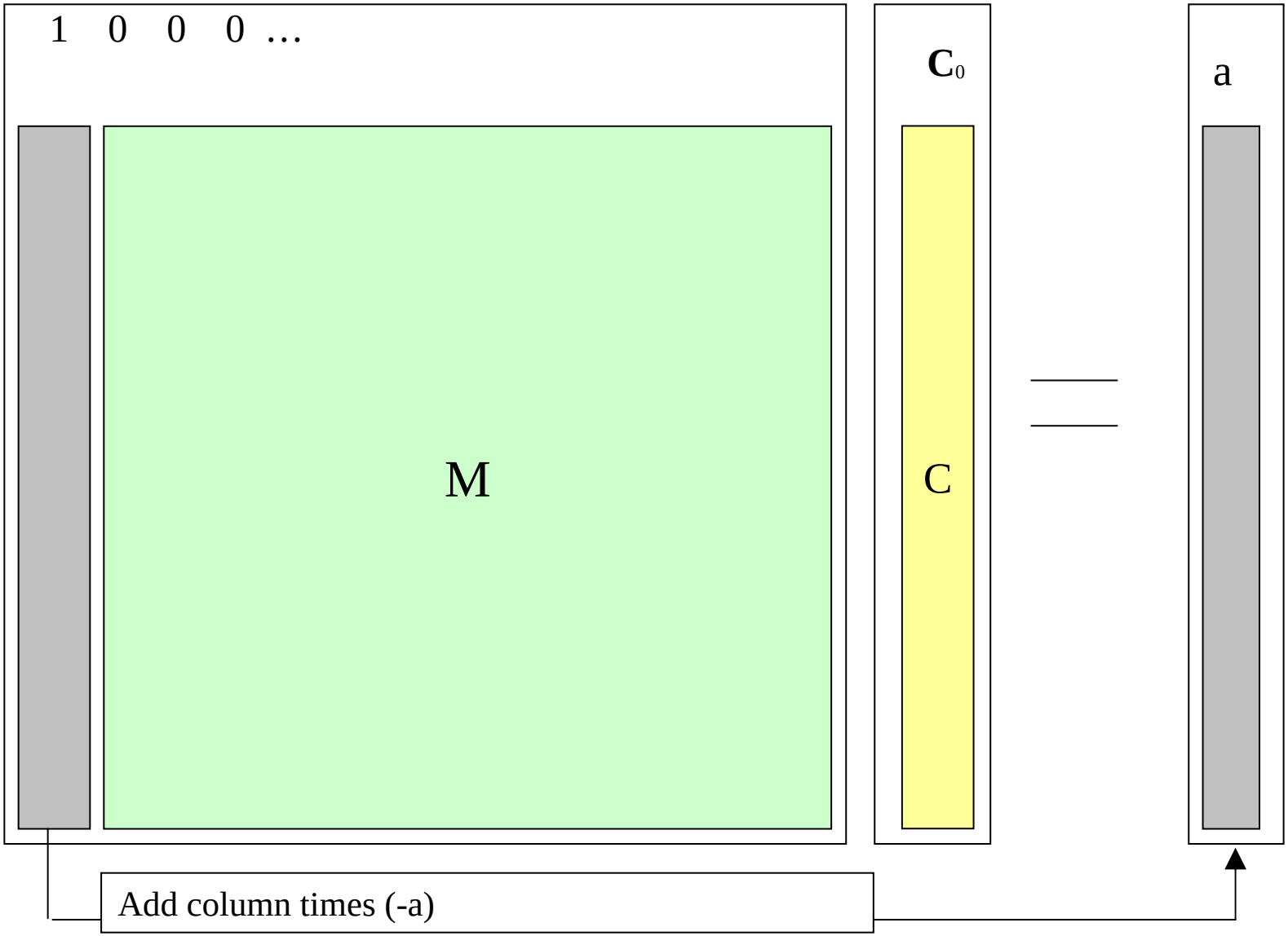


Galerkin's method leads to discretized diffusion equations. Now apply BC and solve linear equations.

$$M_{\alpha\beta} C_{\beta} = r_{\alpha}$$

Matrix equations are solved using sparse matrix methods.

Implementing BCs : Applying Matrix “Benediction”



Computational Issues

- We have three diffusion equations for ternary diffusion, only two being relevant if mass conservation holds.
- We use Hermite interpolation polynomials with 2 or 3 nodes per element:
  - 4 x 4 or 6 x 6 element matrices
  - With 2 equations for the 2 independent concentrations, we have 8 x 8 element matrices.
  - Each diffusion partition may need 3~10 elements. If there are 10 partitions in the diffusion region, we have 30~100 elements, and a global matrix of dimension: 30x2 +2 = 62 to ~202.
- So the FEM computational aspects are “managable.”