Square–Root Diffusivity Method

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Outline

- Introduction: Importance of multicomponent diffusion in alloys
- Composition space, matrix diffusivity, and Euler angles.
- Linearly independent solutions to Fick's law: 1-d, single phase,
- Square-root diffusivity method: A systematic approach.
- *Profiler* and RPI's MatLab© codes for handling linear algebra.
- Typical results:
  - Penetration curves
  - Diffusion paths
  - Special Euler angles
  - Fluxes and ZFP's
  - Near-Collocation of ZFP's
- Near collocation of ZFP's, minimizing multicomponent transport.

Square-Root Diffusivity Matrix

- For a ternary alloy, containing *n*=3 components, the intrinsic diffusivity matrix is

$$D_{ij} \qquad \begin{matrix} D_{11} & D_{12} & D_{13} \\ D_{21} & D_{22} & D_{23} \\ D_{31} & D_{32} & D_{33} \end{matrix}$$

and Fick's law becomes

$$\mathbf{J}_i \qquad D_{ij} \quad C_j$$

- Grube–Jedele solution to Fick's second law for an infinite diffusion couple

$$C(x,t) \qquad \frac{C_0}{2}\mathrm{erfc}$$

where similarity variables, ξ_i, may be defined for multicomponent diffusion,

$$_i \qquad \frac{x}{\sqrt{4E_i t}} \qquad (i \quad n \quad 1)$$

Square-Root Diffusivity Matrix

• The square-root diffusivity matrix, [r_{ij}], is related to the diffusivity matrix, [D_{ij}], as

$$D_{ij} \quad r \quad r$$

• The matrix [r_{ij}] must be positive-definite, with eigenvectors identical to those of the diffusivity, [D_{ij}]. For ternary alloys, this expression expands as

$$\begin{array}{cc} D_{11} & D_{12} \\ D_{21} & D_{22} \end{array} \qquad \begin{array}{cc} r_{11} & r_{12} \\ r_{21} & r_{22} \end{array} \qquad \begin{array}{cc} r_{11} & r_{12} \\ r_{21} & r_{22} \end{array}$$

Square-Root Diffusivity Matrix

- The algebraic steps used to extract [r_{ij}] from [D_{ij}] are the following:

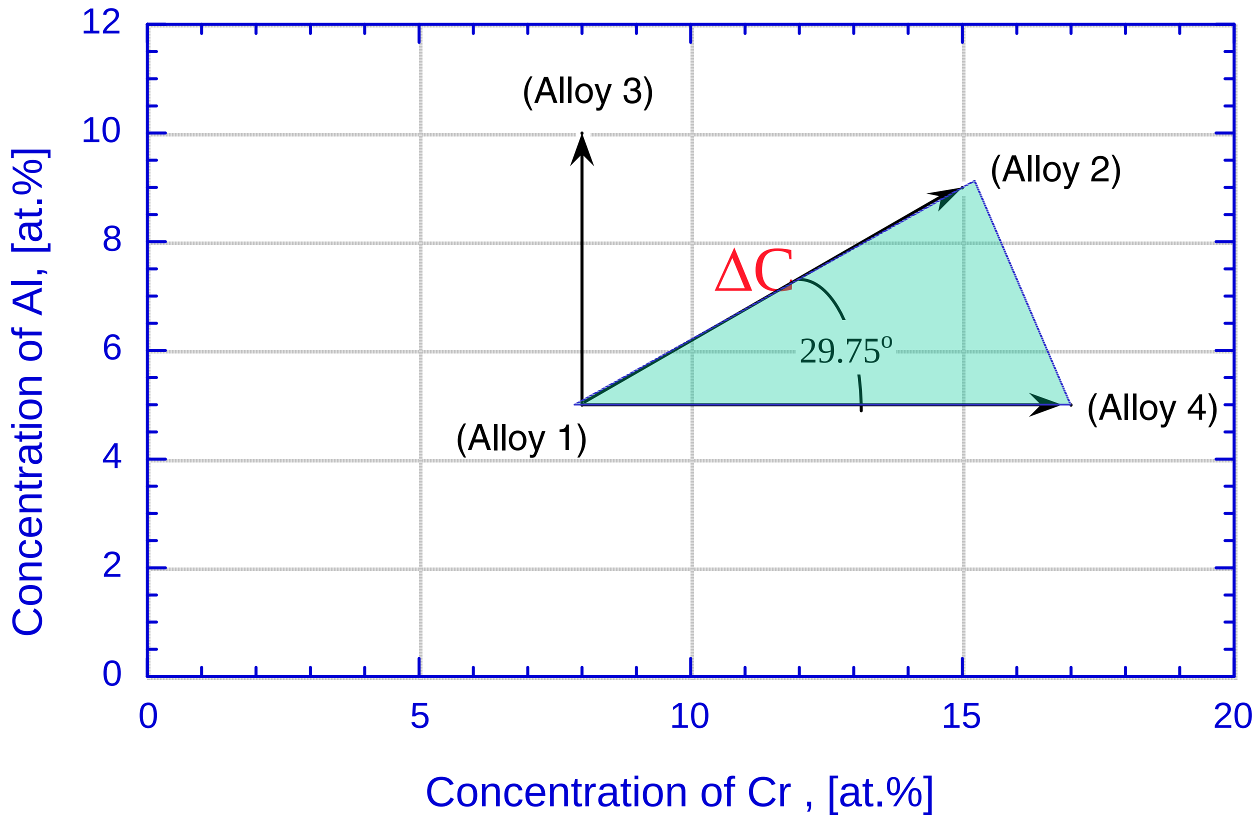
    i. The eigenvectors and eigenvalues of the initial matrix [D_{ij}] form a diagonal matrix, [E_{ij}], and a transformation matrix, [α_{ij}].

    ii. The square root of [E_{ij}] is determined by taking the square roots of its eigenvalues.

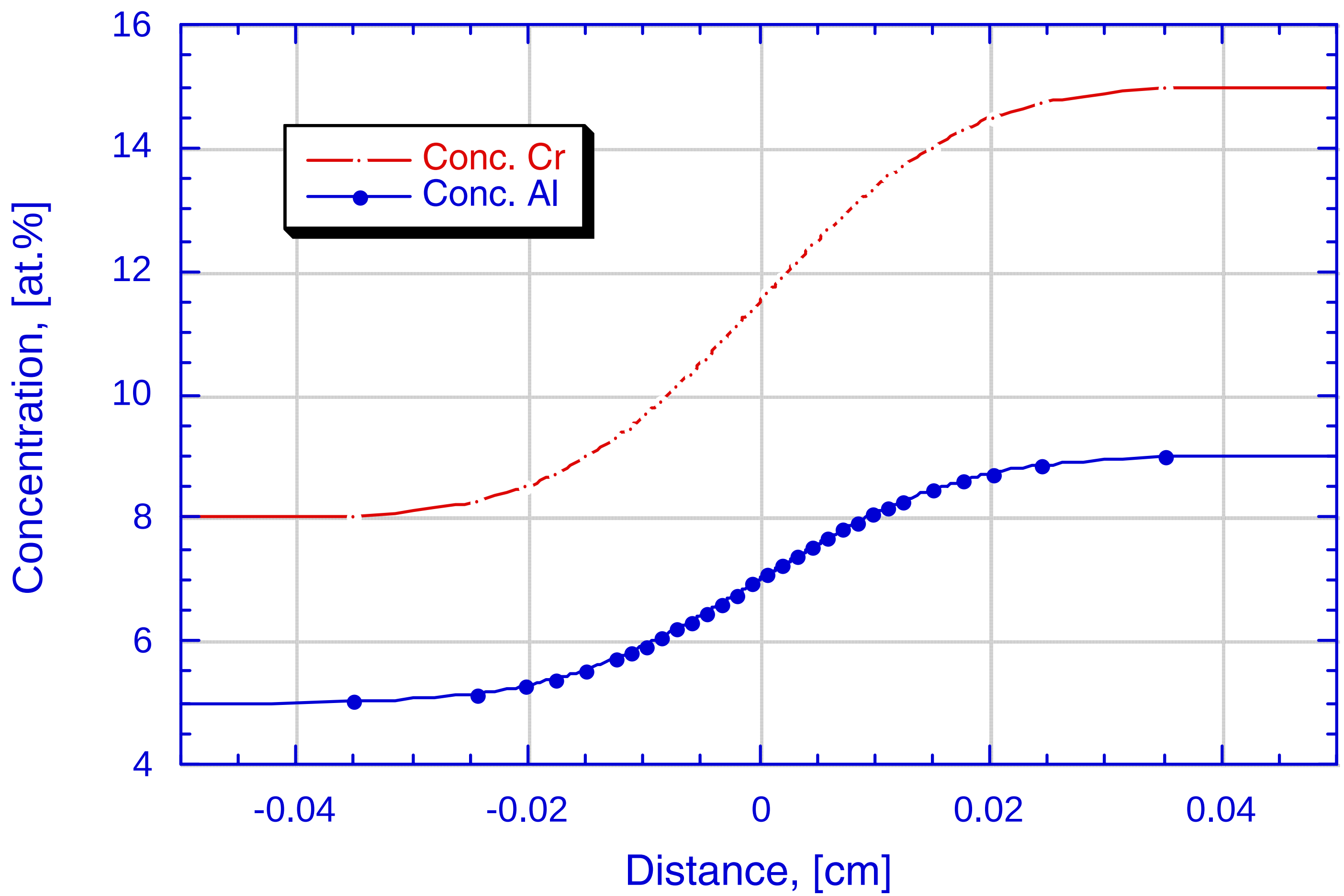
    iii. The square-root diffusivity matrix [r_{ij}] is obtained from the initial matrix.

$$D_{ij}{}^{\frac{1}{2}} \qquad {}_{ij} \qquad E_{ij}{}^{\frac{1}{2}} \qquad {}_{ij}{}^{\;1} \qquad r$$

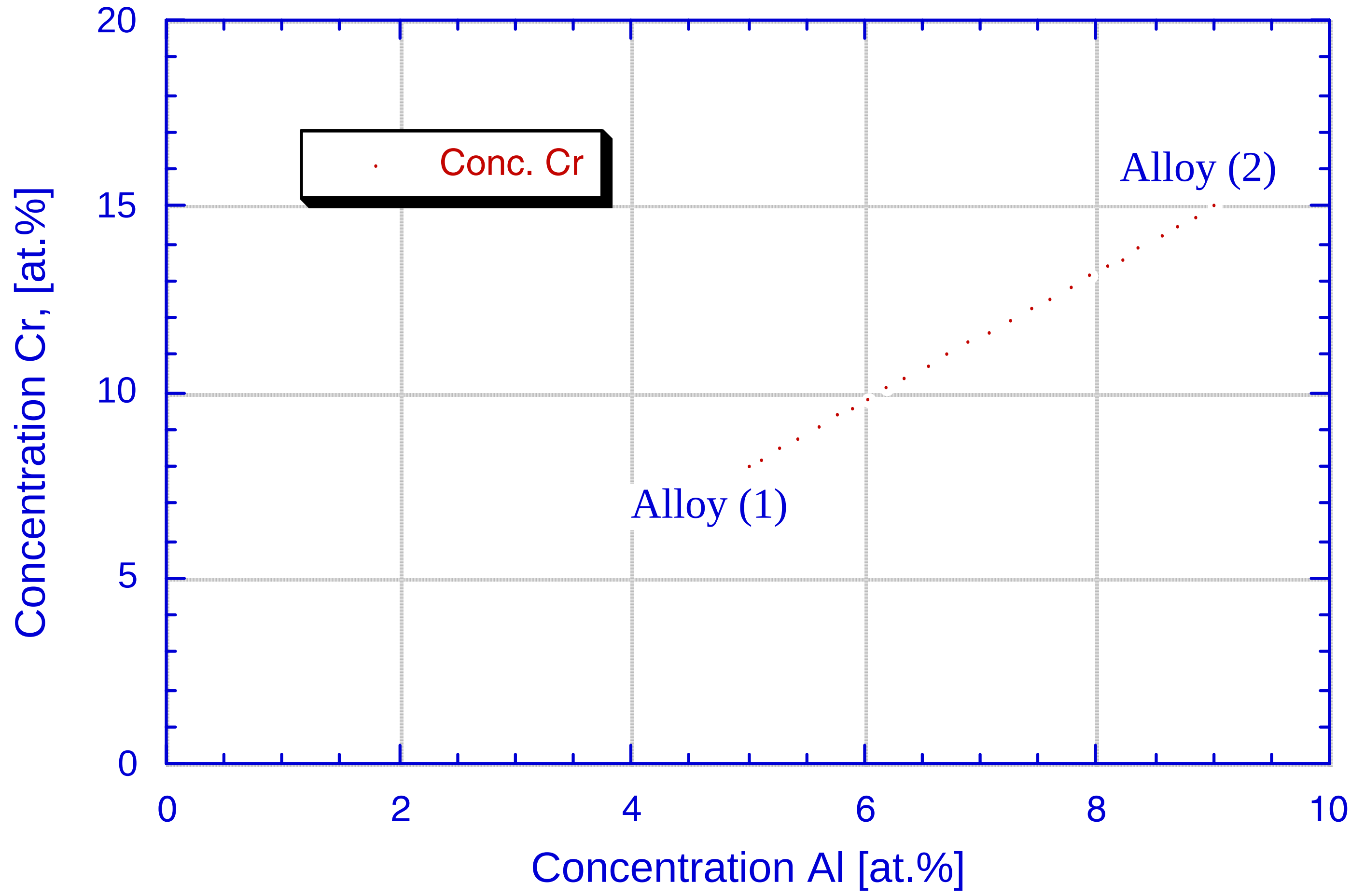
Composition Space



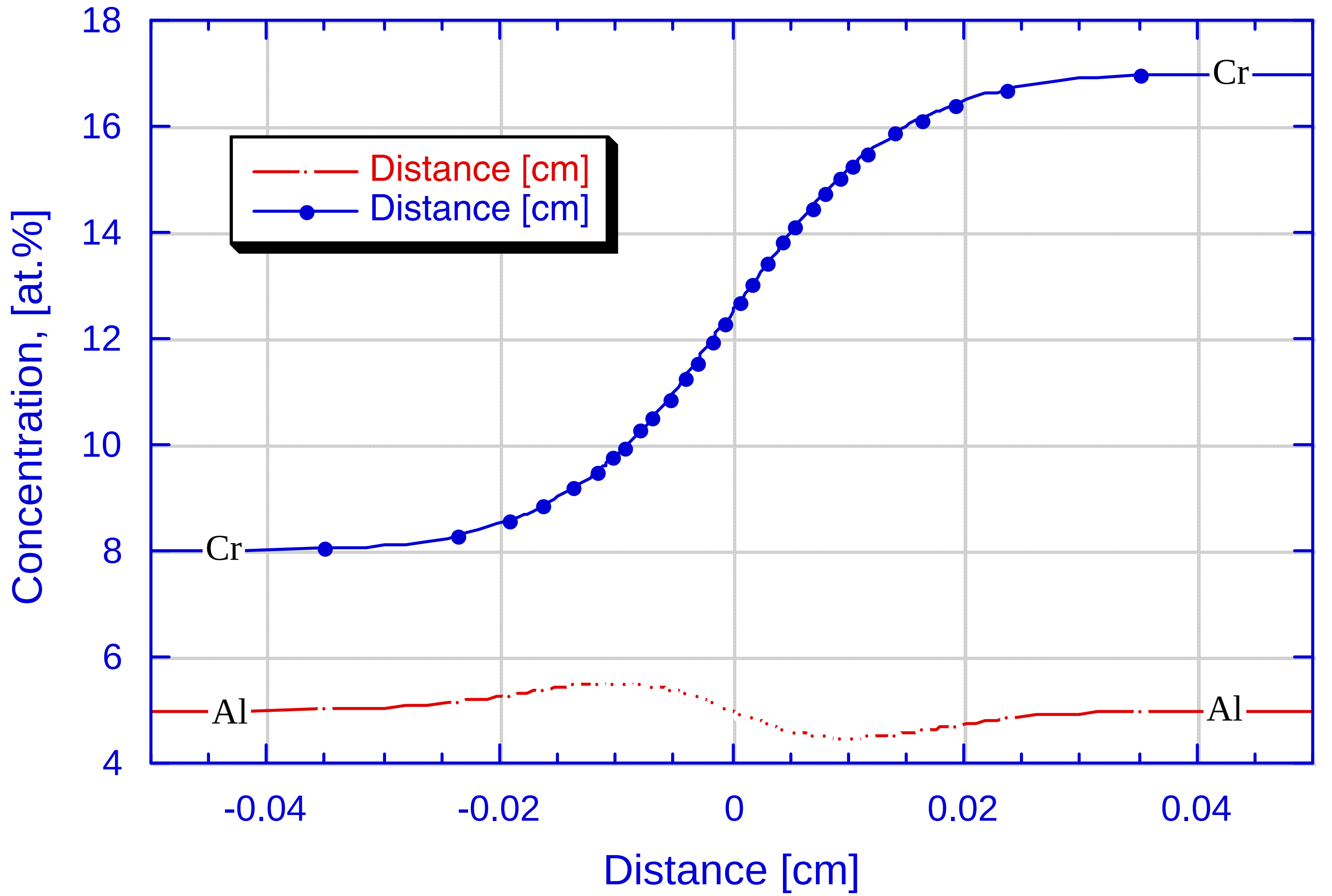
Concentration versus distance



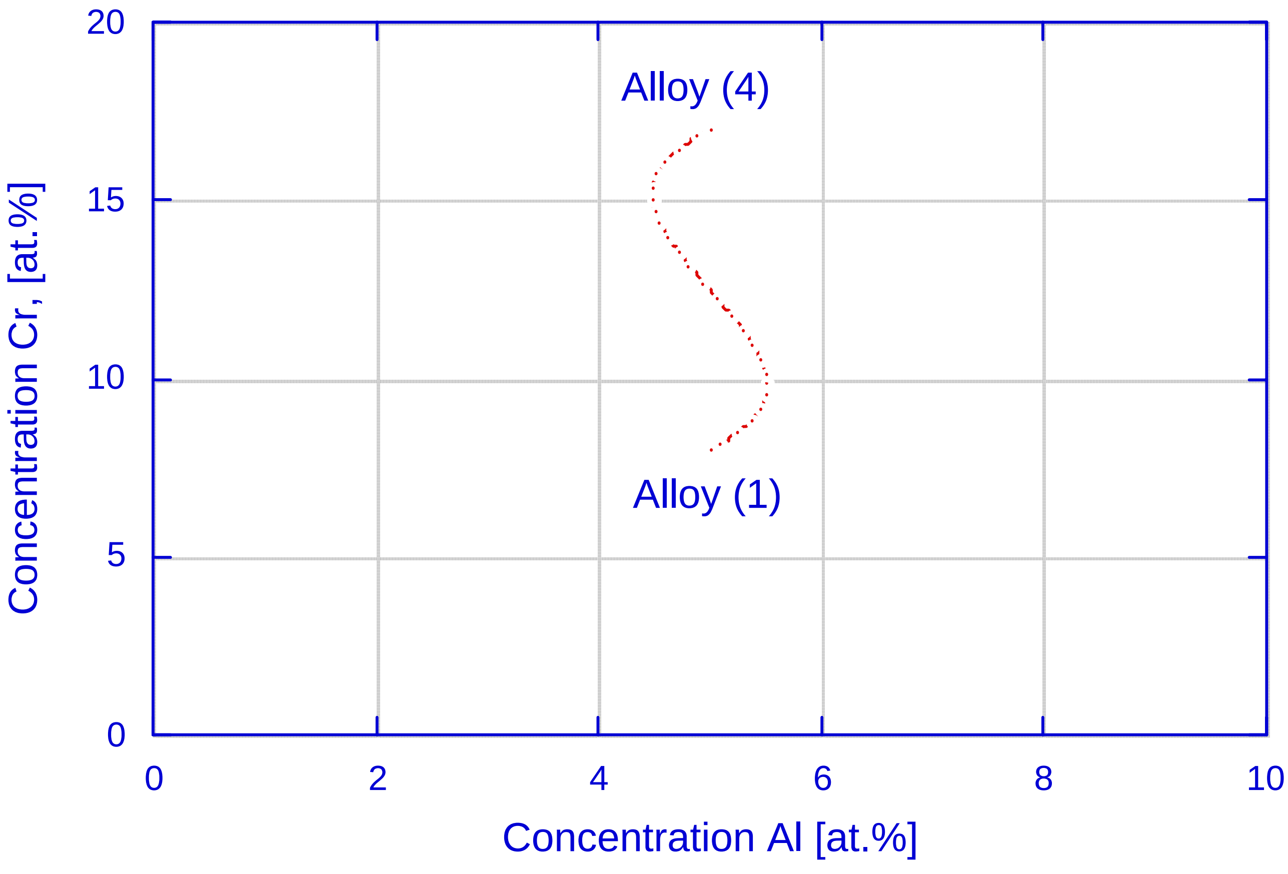
Diffusion Path



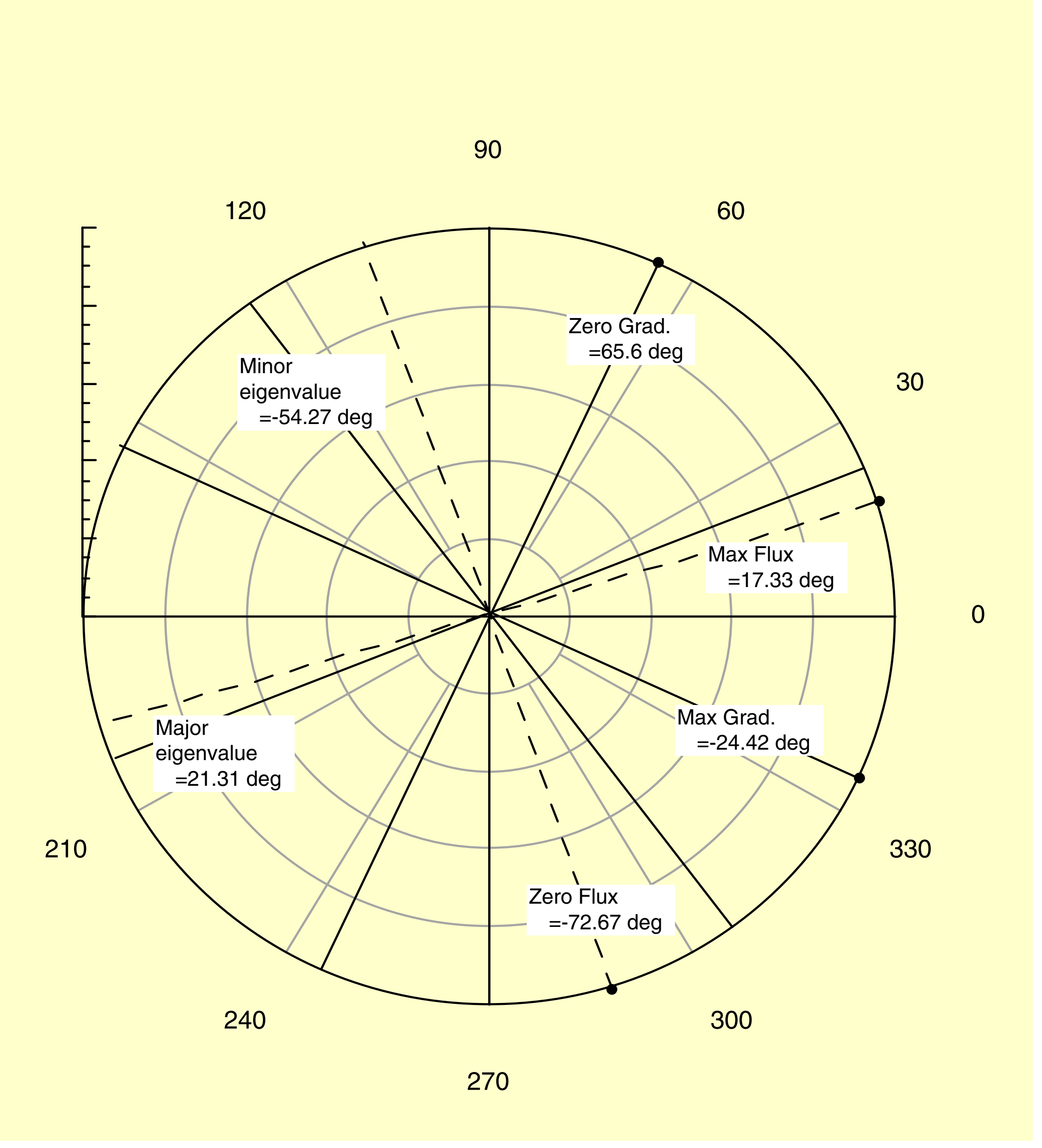
Concentration versus distance



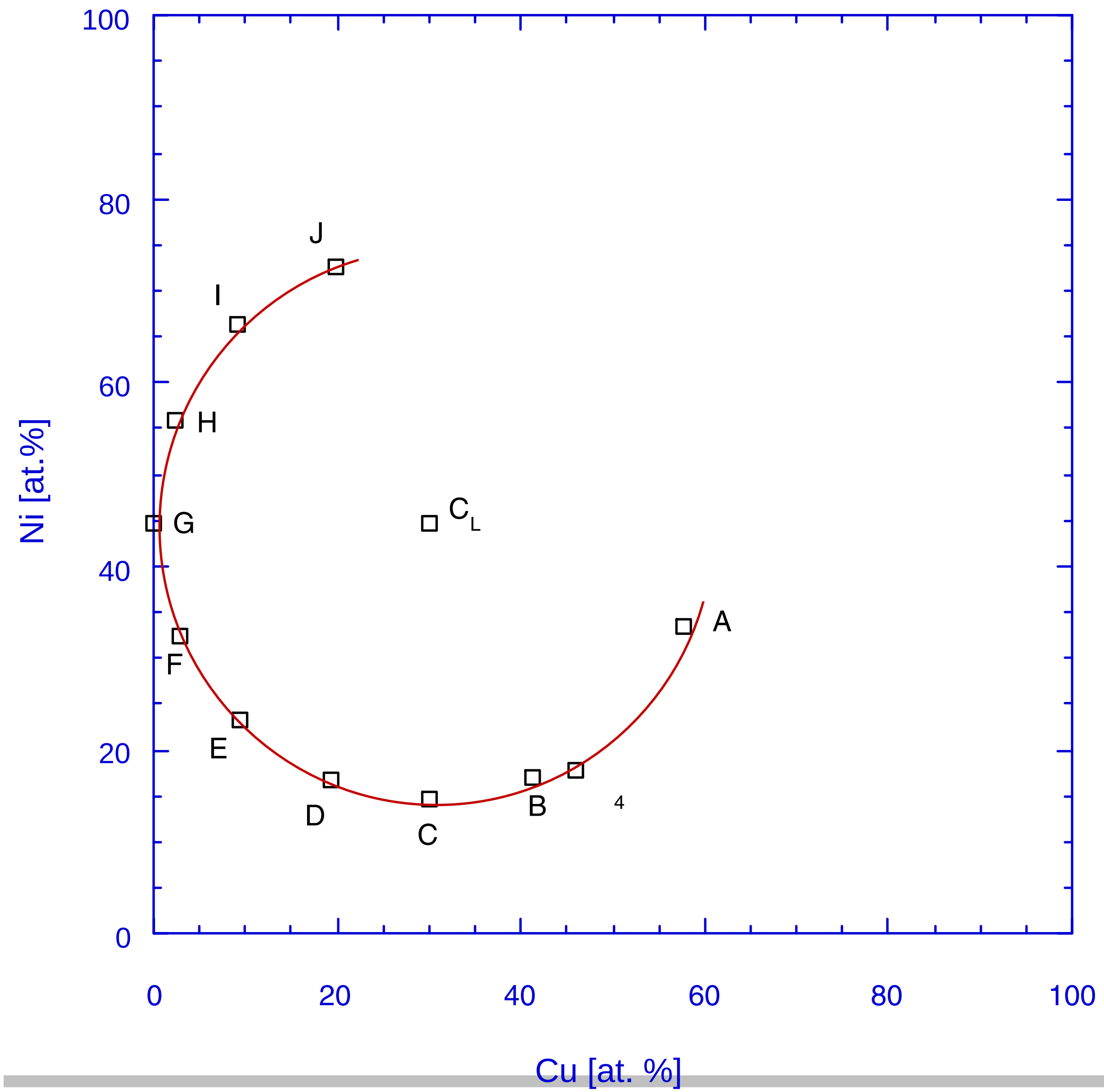
S-shaped Diffusion Path



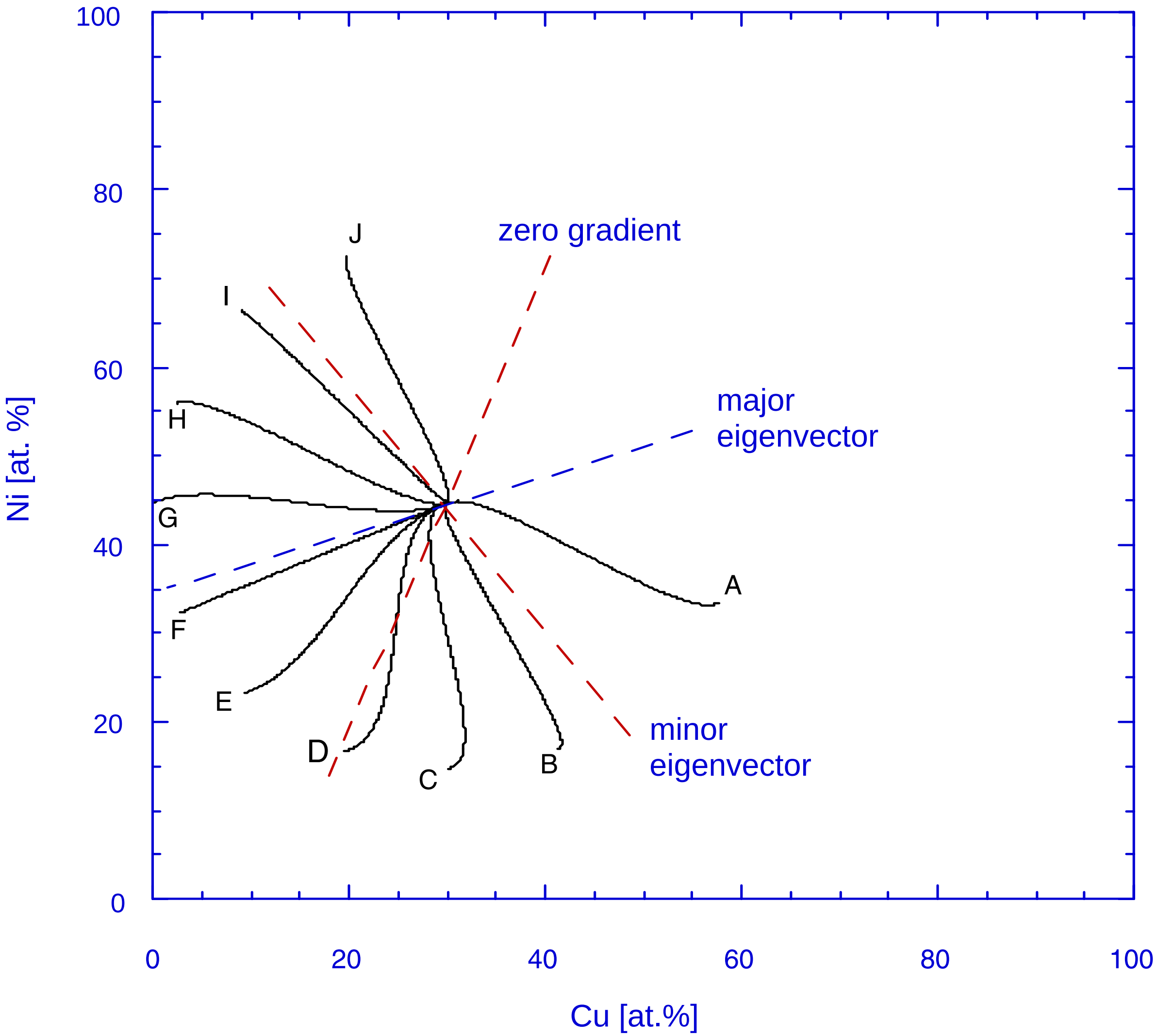
Orientations in Composition Space



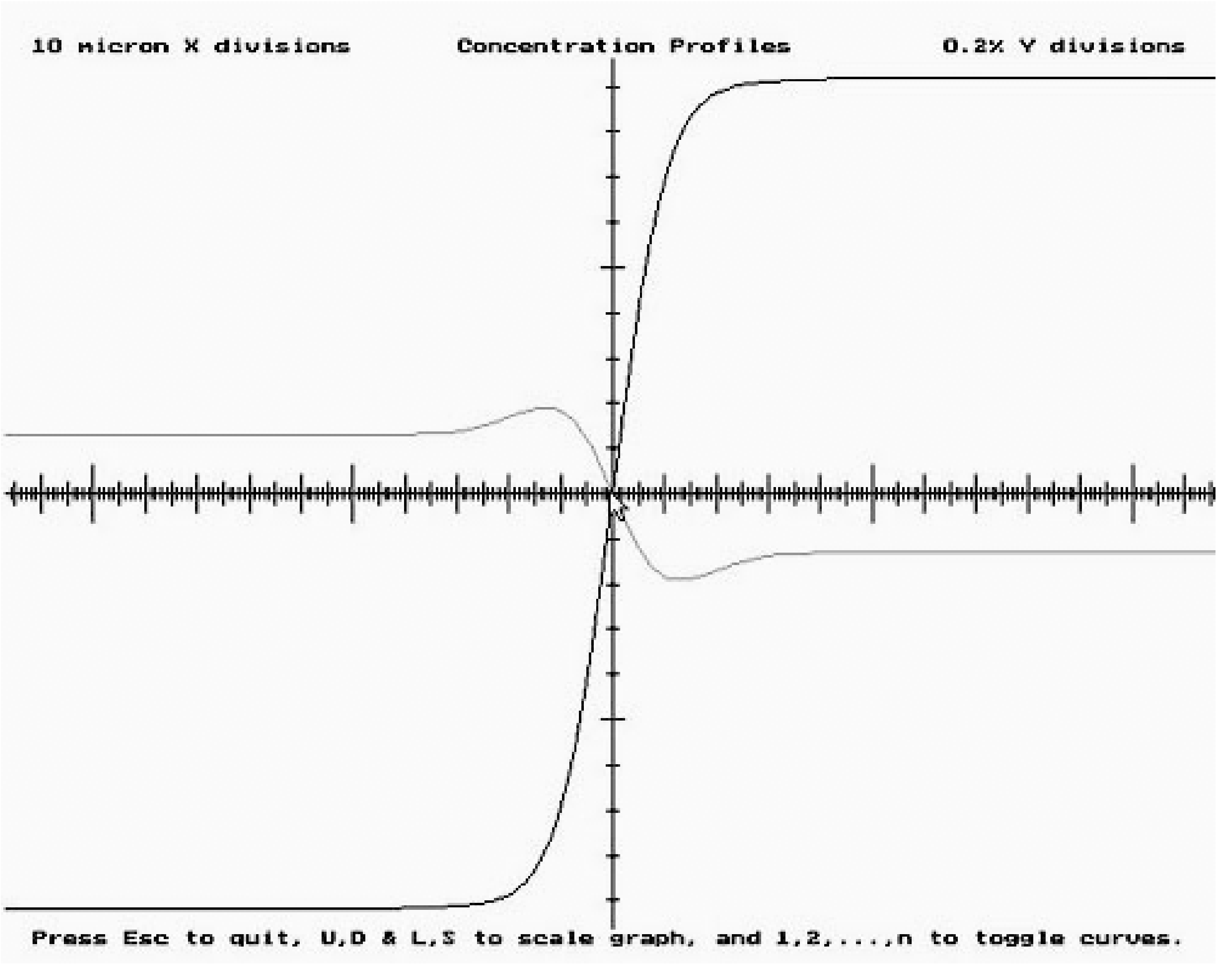
Locus of Alloy Compositions



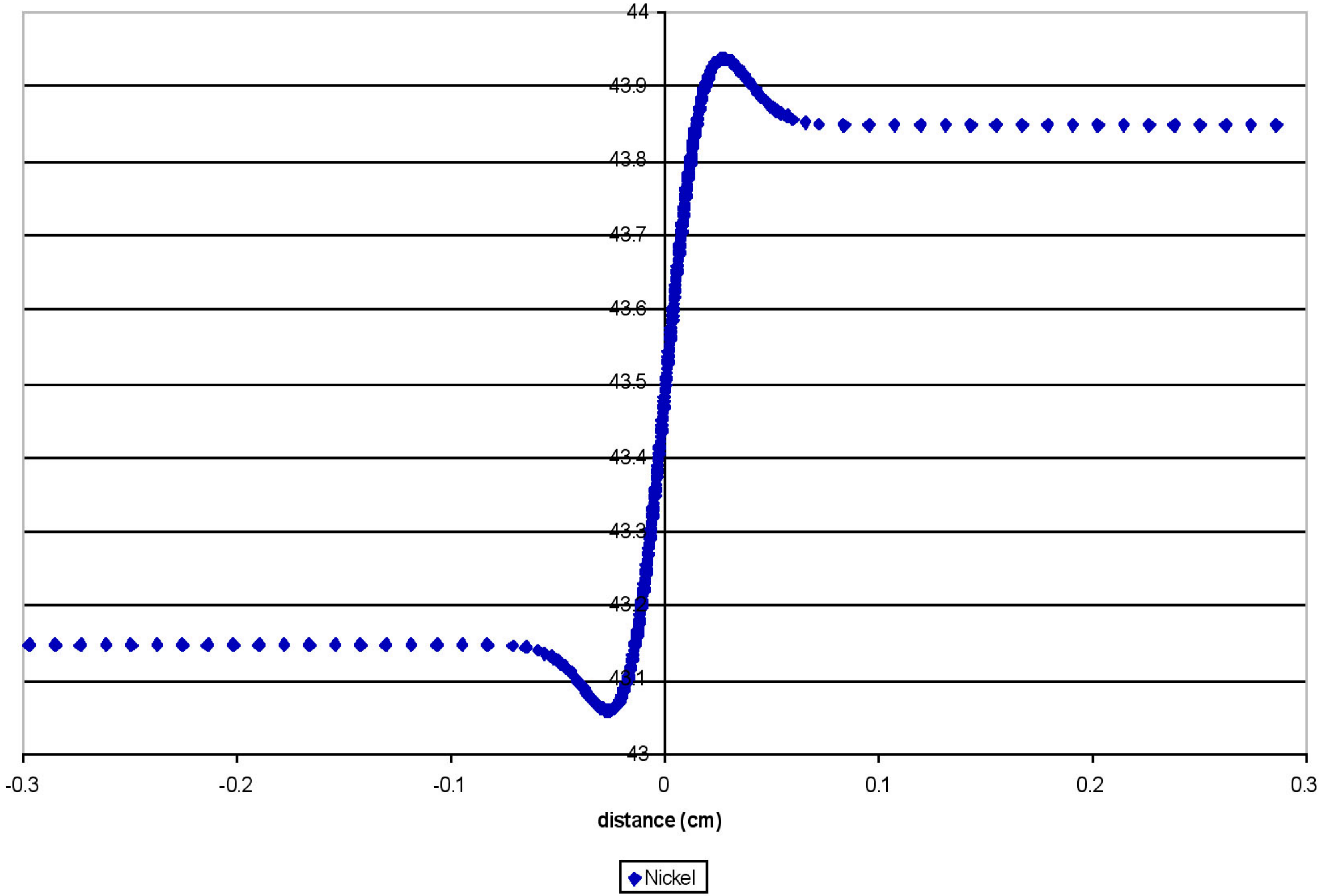
Multicomponent Diffusion Paths



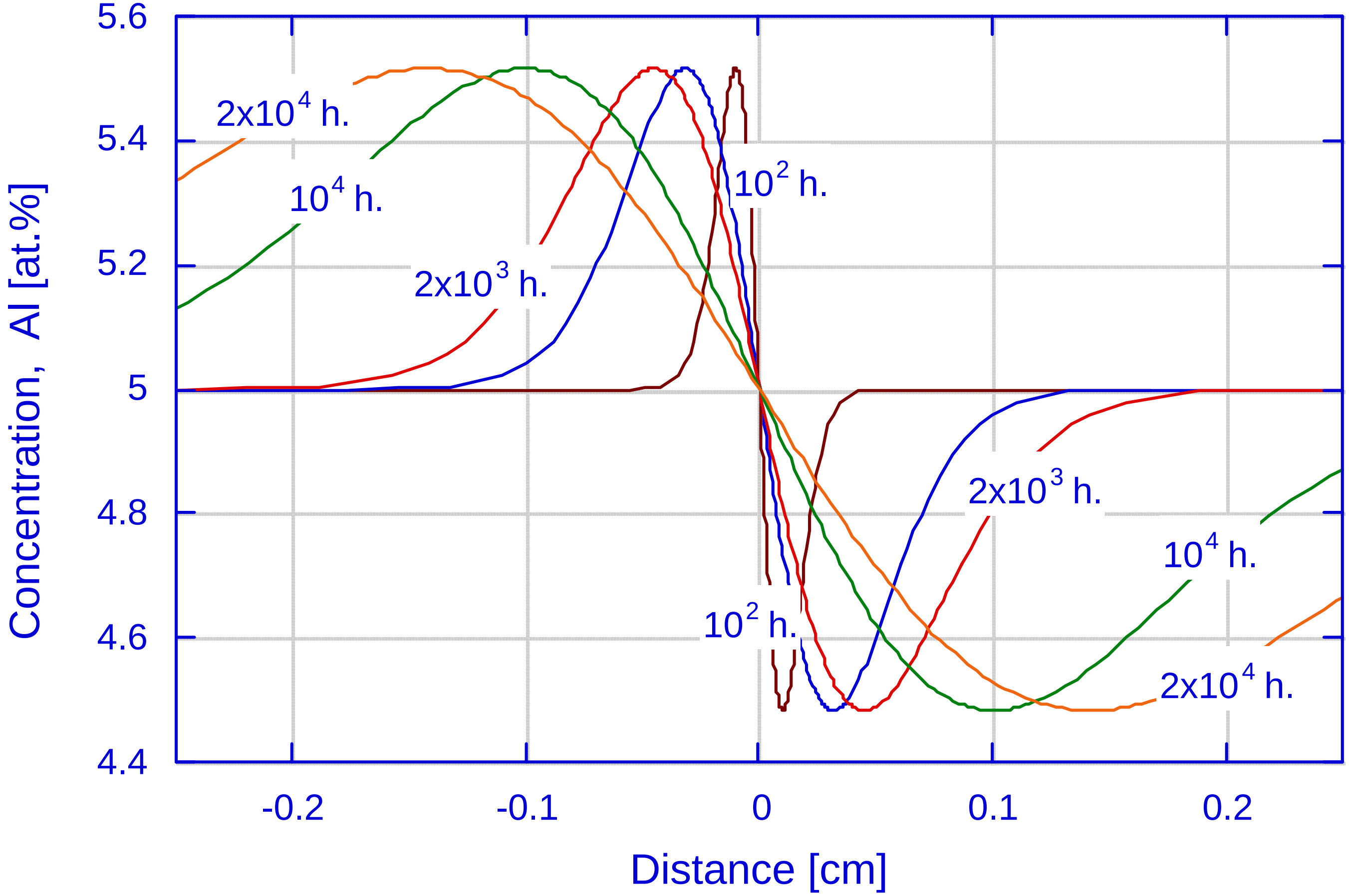
Profiler Screen Profiles



Profiler output: Up-hill Diffusion



Time-Dependence of Penetration Curves



RPI's Matlab© Code: Flux Equations

Acta Materialia, **51**, 1181-1193, 2003.

$$J_1 \qquad C^o \quad \frac{D_{11}}{\sqrt{\ t}} \; \frac{A_{11}}{e_1} e^{\frac{x^2}{4e_1^{\,2}t}} \qquad \frac{A_{12}}{e_2} e^{\frac{x^2}{4e_2^{\,2}t}} \qquad \frac{D_{12}}{\sqrt{\ t}} \; \frac{A_{21}}{e_1} e^{\frac{x^2}{4e_1^{\,2}t}} \qquad \frac{A_{22}}{e_2} e^{\frac{x^2}{4e_2^{\,2}t}}$$

$$J_2 = \Delta C^\circ \left(-\frac{D_{21}}{\sqrt{\pi t}} \left(\frac{A_{11}}{e_1} e^{-\frac{x^2}{4e_1^{\,2}t}} + \frac{A_{12}}{e_2} e^{-\frac{x^2}{4e_2^{\,2}t}} \right) - \frac{D_{22}}{\sqrt{\pi t}} \left(\frac{A_{21}}{e_1} e^{-\frac{x^2}{4e_1^{\,2}t}} + \frac{A_{22}}{e_2} e^{-\frac{x^2}{4e_2^{\,2}t}} \right) \right)$$

$$J_3 = -\left(J_1 + J_2\right)$$

Local mass conservation, ternary system

RPI Matlab© Code

10At.%Cr-10%At.Al-80%At.%Ni

- D_{ij} matrix

$$\mathbf{D} \quad \begin{matrix} 12.6 & 7.8 \\ 7.6 & 22.0 \end{matrix} \quad 10^{-11} \quad cm^2/s$$

- Square-root diffusivity matrix

$$\mathbf{r} \quad \begin{matrix} 1.0805 & 0.3080 \\ 0.3001 & 1.4517 \end{matrix} \quad 10^{-5} \quad cm/\sqrt{s}$$

Stationary Zero Flux Planes

- Cr

$$\Psi_{ZFP}^{Cr} = \tan^{-1}\left(-\frac{r_{11}}{r_{12}}\right) \approx -74.09^{\circ},\ 105.91^{\circ}$$

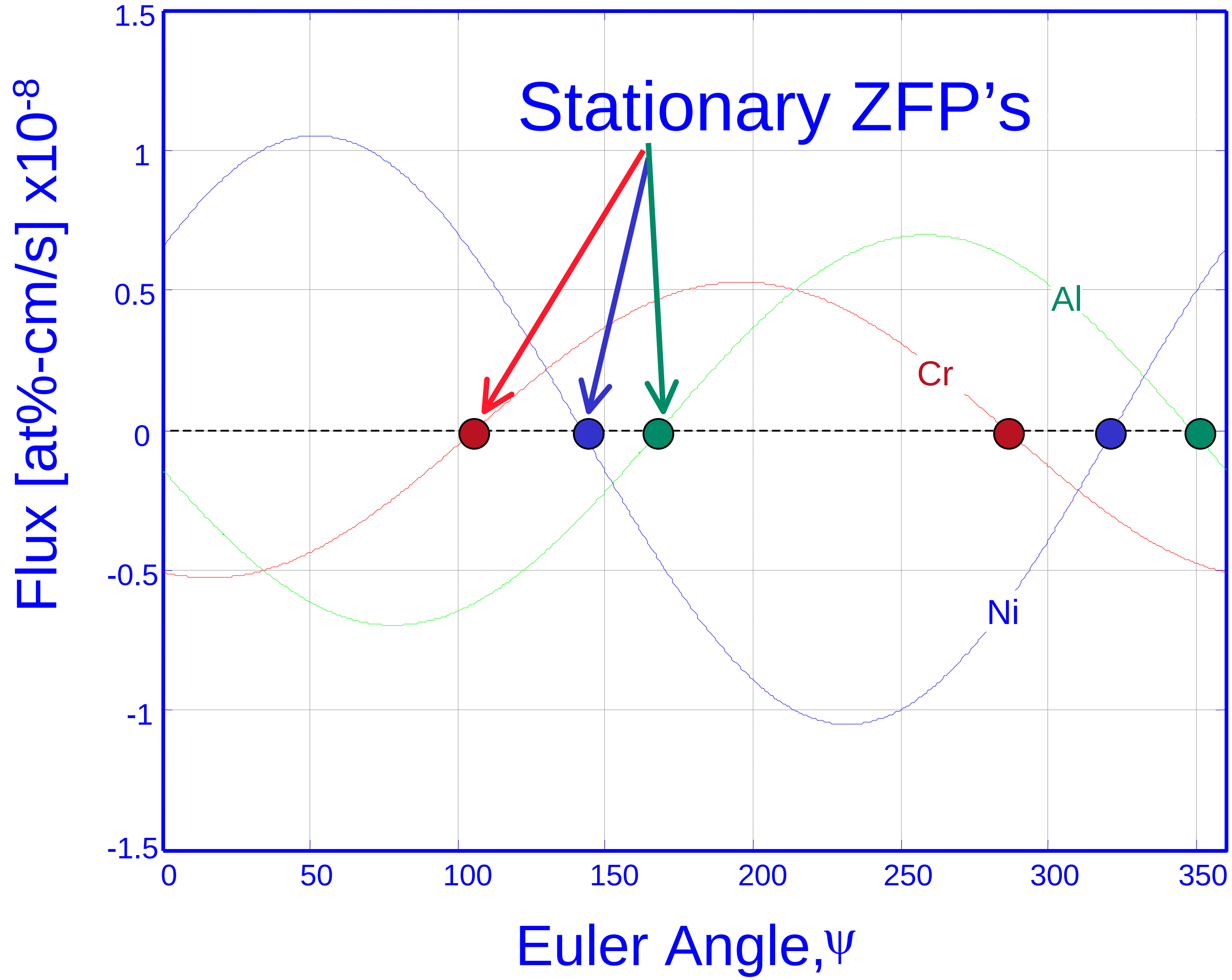
- Al

$$\Psi_{ZFP}^{Al} = \tan^{-1}\left(-\frac{r_{21}}{r_{22}}\right) \approx -11.68^{\circ},\ 168.32^{\circ}$$

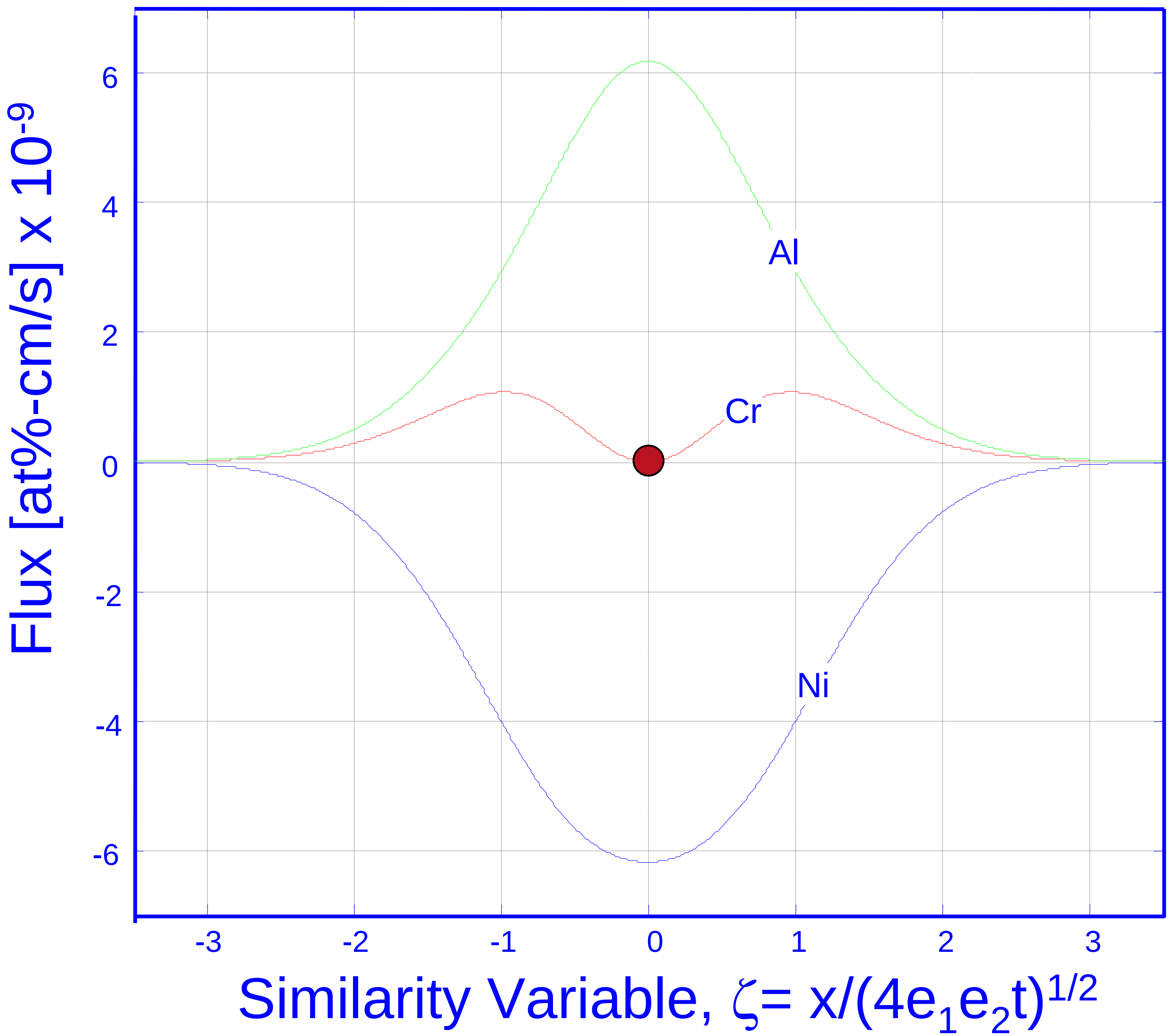
- Ni

$$\Psi_{ZFP}^{Ni} = \tan^{-1}\left(-\frac{r_{11}+r_{21}}{r_{12}+r_{22}}\right) \approx -38.11^{\circ},\ 141.89^{\circ}$$

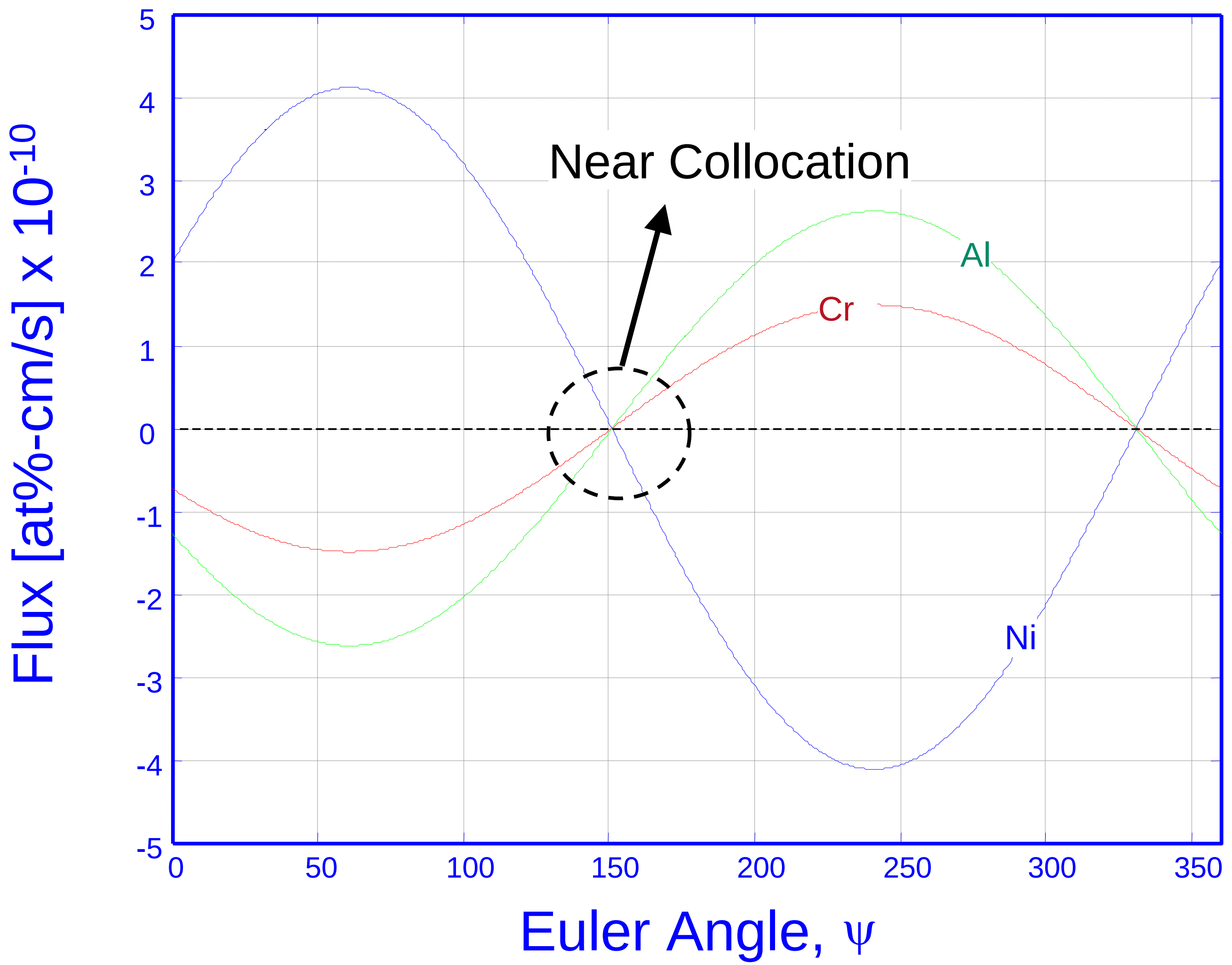
Component Fluxes versus Euler angle, at ζ=0



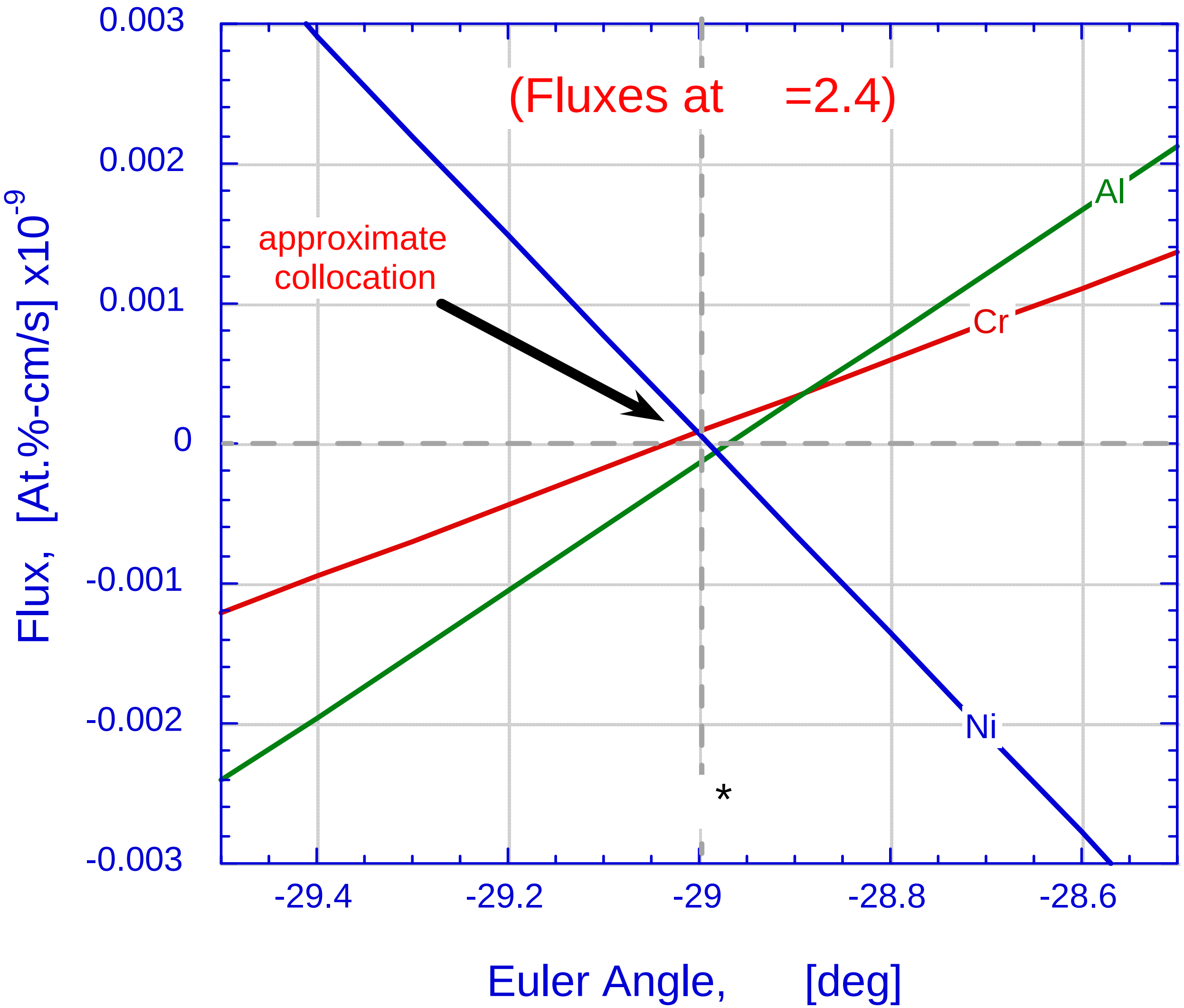
Stationary ZFP for Cr: ψ =-74.09°



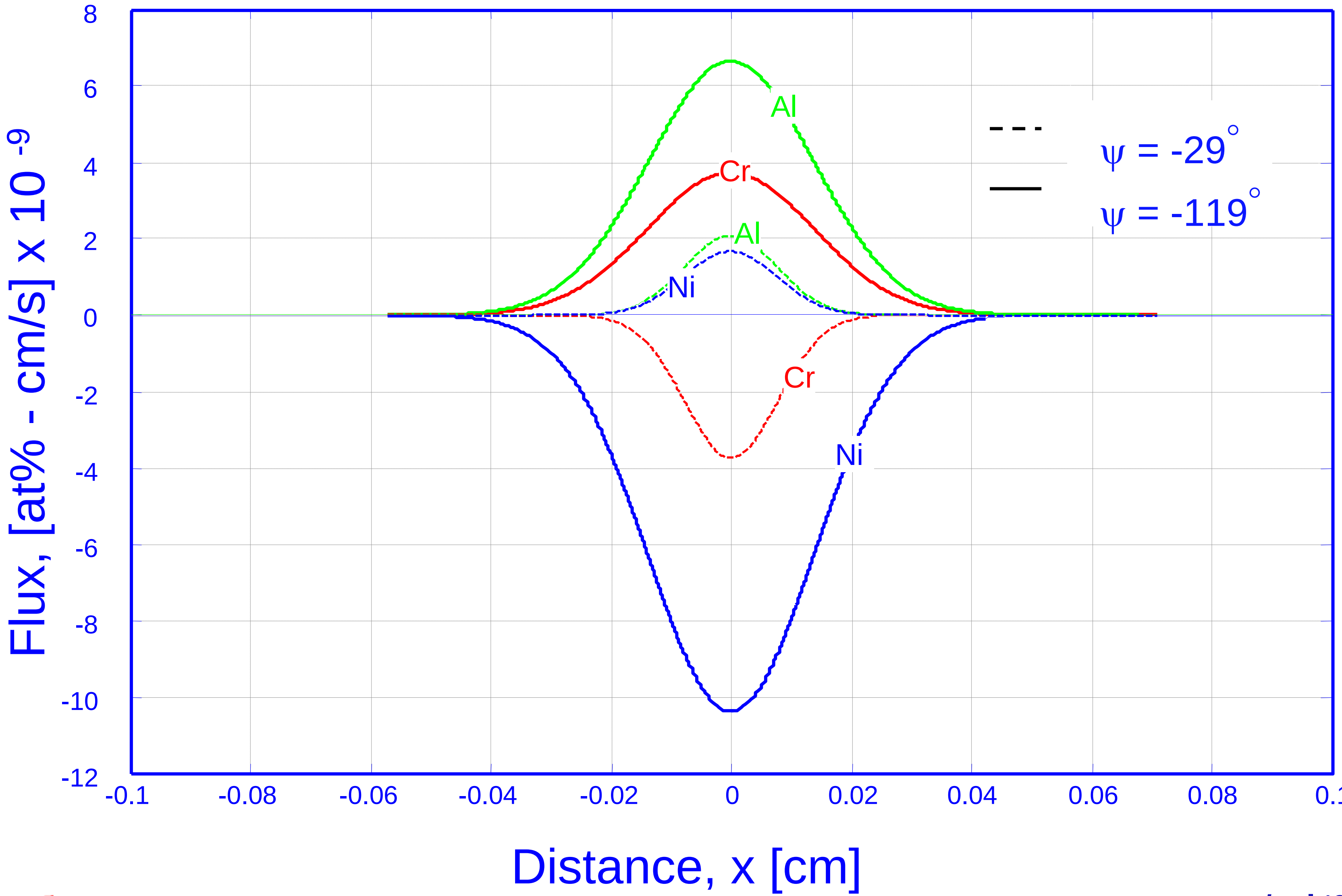
Component Fluxes versus Euler angle, at ζ=2.4



Near-Collocation of ZFP's



Flux versus Distance



Summary

- John Morral and co-workers established the first systematic methodology for quantitative treatment of single-phase, linear multicomponent diffusion.
- This approach provides much insight into the complexities attending “beyond binary diffusion.”
- *Profiler*, a public domain DOS software, was produced in 1990 by John Morral and M.K. Stalker to aid in overcoming the labor of solving the linear algebra required in multicomponent diffusion.
- RPI’s MatLab code provides a similar approach linked to a modern computational and graphics platform.
- Materials students can now easily learn the rudiments of higher-order diffusion, and use these techniques as part of their professional “tool kit.”