Modeling Marker Motion in Diffusion Couples

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Exploration of marker motion in 1-D single phase & multiphase diffusion couples
w/ concentration dependent diffusivities

Three computational methods:

• Similarity variable: NSolution by shooting method with matching error function in far fields ~ Jeff
• DICTRA ~ Carrie
• Diffuse Interface (Cahn-Hilliard); NSolution by *FiPy* - finite volume ~ Jon

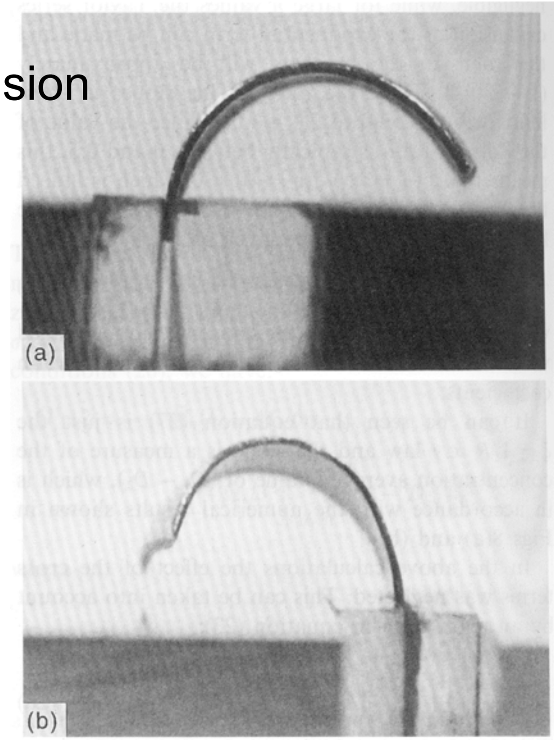
• Kirkendall markers sometimes become dispersed slightly in the diffusion direction. Other times them remain sharply concentrated. (VanLoo et al., Höglund & Agren)
• Kirkendall markers occasionally end up at two different places. This has only been seen in couple with moving interfaces. (VanLoo et al.)
• A. Paul et al. observed markers in two positions within NiAl in a multiphase diffusion couple

Why do we care?

Stress and deformation in thin films subject to reaction diffusion

"Diffusion Induced Bending of Thins Sheet Couples: Theory and Experiment for Ti-Zr," I Daruka et al. Acta Mater. 44(1996), 4981-4993.

- 0.1 mm thick bonded Ti & Zr sheets
- 2-5 hrs anneal @1183, 1233, 1273 K
- Radius as small as 4 mm
- $D_{Zr}-D_{Ti}$ = 5 x10^{-14} m^2/s
- $\tilde{D}$ = 1.7 x 10^{-13} m^2/s
- Difference in partial molar volumes is small



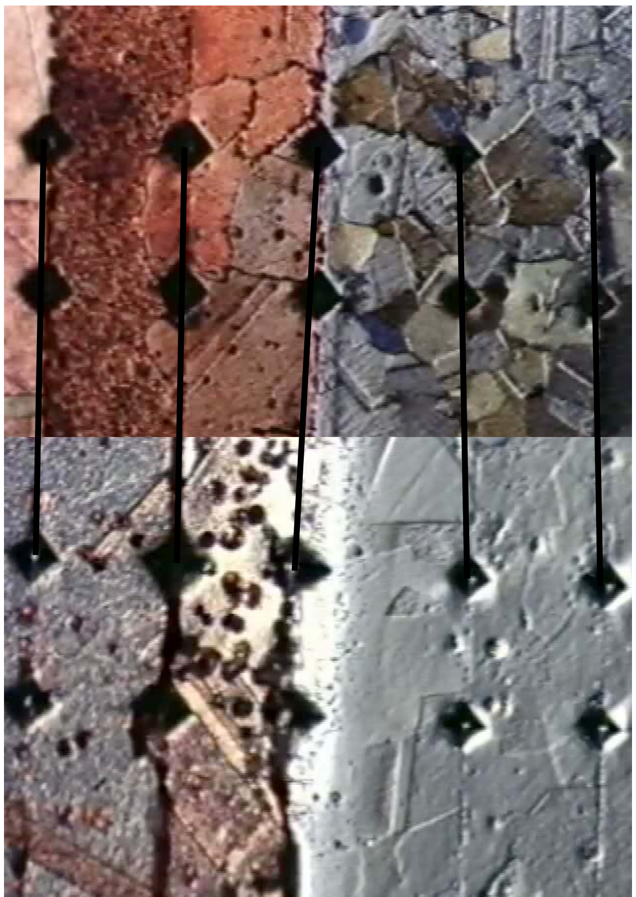
Similar experiments
Cu-Ni and other systems

A consideration of deformation accompanying reaction diffusion helps clarify….

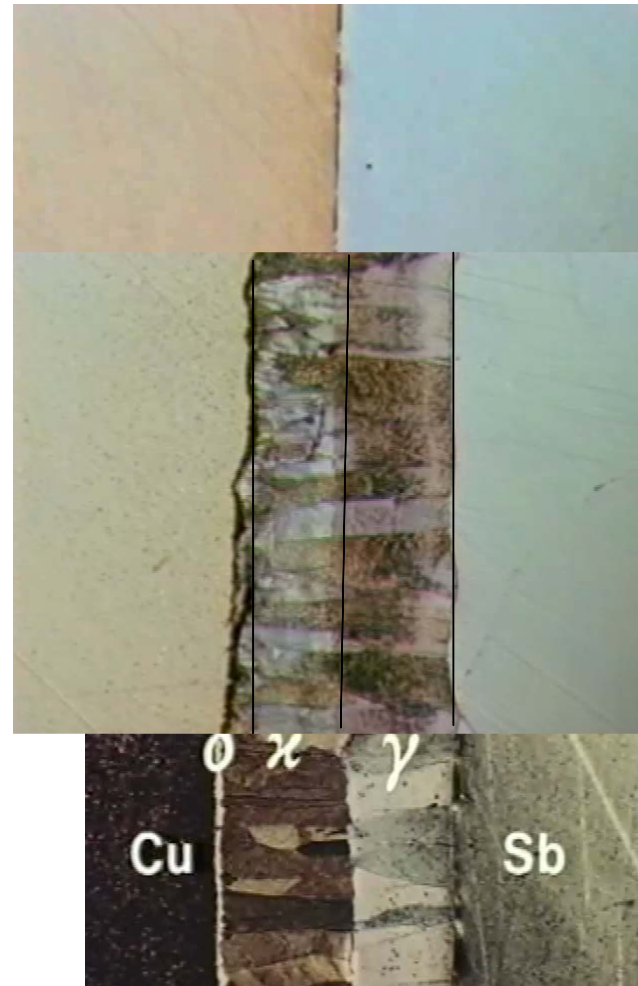
In continuum mechanics approaches to deformation in solids, one employs a reference configuration and actual configuration. What is the relation ship between these and the terms usually employed in diffusion theory; viz., Lattice fixed frame=?marker frame, volume fixed frame=? lab frame.

Films: “Diffusion in Solid Metals: Single-phase Systems”
“Diffusion in Solid Metals: Multiphase-Diffusion
T. Heumann & V. Ruth

Cu



Ni



Marker motion

Cornet and Calais (1972)

Get marker velocity from
- concentration profile
- value of $\Delta D = D_B - D_A$

$$\mathrm{v}(z,t) = \Delta D(X_B)\frac{\partial X_B(z,t)}{\partial z}$$

Marker Trajectories

$$\frac{dz(t)}{dt} = \mathrm{v}(\mathrm{z}(\mathrm{t}), \mathrm{t})$$

$$z(0) = \begin{cases} 0 \text{ for "Kirkendall Plane"} & \mathrm{z_K}(\mathrm{t}) \\ \mathrm{z_0} \text{ for "other markers"} & \end{cases}$$

If similarity solution applies

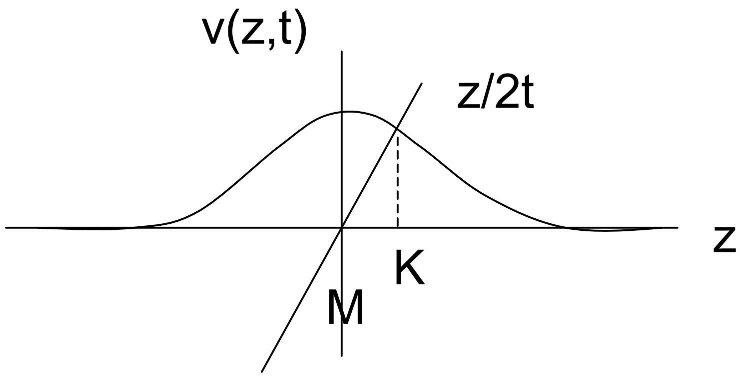
$$z_K(t) = A_K\sqrt{t}$$

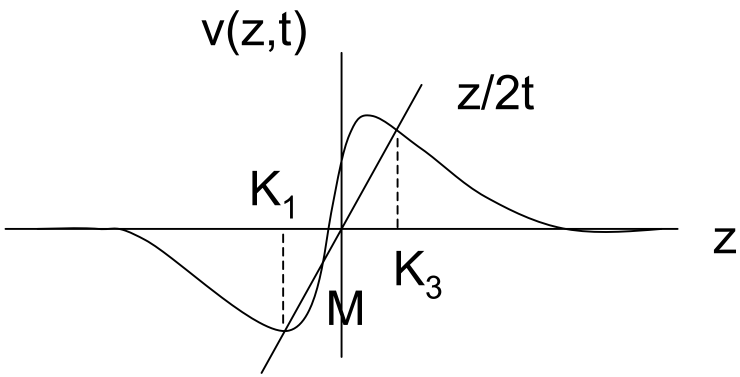
$$\frac{dz_K(t)}{dt} = \frac{A_K}{2\sqrt{t}} = \frac{z_K(t)}{2t}$$

$$\frac{z_K(t)}{2t} = \mathrm{v}(z_K(t), t)$$

Leads to graphical interpretation!

Graphic interpretation of of Kirkendall Plane Location





Questions

- How do a set of markers move when there are multiple Kirkendall planes?
- How do a set of markers move when there is a moving interface?
- How do these conclusion depend on the sharp interface model?
- Can we compute marker motion using a diffuse interface model of a moving interface?
- What kind of stresses might be generated by these effects?

$$J_i = -\frac{M_i X_i}{V_m} \nabla \mu_i; \qquad \nabla = \frac{\partial}{\partial z}$$

$$\tilde{J}_B = -\tilde{J}_A = J_B + \mathrm{v}^M \frac{X_B}{V_m}$$

$$\frac{1}{V_m}\frac{\partial X_B}{\partial t} = -\frac{\partial}{\partial z}\left[\tilde{J}_B\right]$$

$$\tilde{J}_B = -\frac{\tilde{M}}{V_m}\nabla\left[\mu_B - \mu_A\right]$$

$$\tilde{M} = X_A X_B\left[X_B M_A + (1 - X_B) M_B\right]$$

$$\mathrm{v}^{\mathrm{M}} = X_A X_B\left[M_B - M_A\right]\nabla\left(\mu_B - \mu_A\right)$$

Cahn-Hilliard Gradient Energy Model

Sharp Interface Model

$$\mu_B - \mu_A = -\Omega\left(X_B - X_A\right) + RT\left(\ln X_B - \ln X_A\right) - 2K\frac{\partial^2 X_B}{\partial z^2}$$

Interface phase compositions implicit

$$\mu_B - \mu_A = -\Omega\left(X_B - X_A\right) + RT\left(\ln X_B - \ln X_A\right)$$

Plus explicit imposition of interface phase compositions

$$\tilde{J}_B = -\frac{\tilde{D}}{V_m}\nabla X_B \qquad \frac{\partial X_B}{\partial t} = \frac{\partial}{\partial z}\left[\tilde{D}\frac{\partial X_B}{\partial z}\right]$$

$$\tilde{D} = \tilde{M}\left[\frac{RT}{X_A X_B} - 2\Omega\right] = \left[X_B M_A + X_A M_B\right]\left[RT - 2\Omega X_A X_B\right]$$

$$= D_A X_B + D_B X_A$$

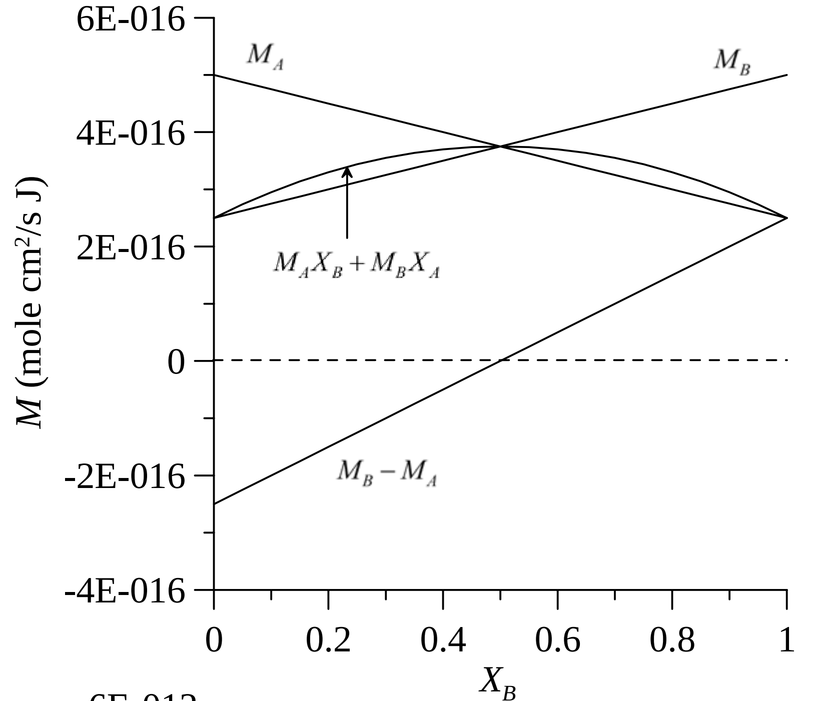
$$\mathrm{v}^{\mathrm{M}} = \left[M_B - M_A\right] RT\left\{1 - \frac{2\Omega}{RT} X_A X_B\right\}\nabla X_B$$

$$= \left[D_B - D_A\right]\nabla X_B$$

$$D_A = M_A RT\left[1 - \frac{2\Omega}{RT} X_A X_B\right] \text{ and } D_B = M_B RT\left[1 - \frac{2\Omega}{RT} X_A X_B\right]$$

Thermodynamic and Kinetic parameters

Chosen to permit:
- Miscibility gap
- Opposite Kirkendall effects in the two phases



$$M_A = M_0\left[\beta_1(1-X_B)+\beta_2 X_B\right] \quad m^2 mole/Js$$

$$M_B = M_0\left[\beta_2(1-X_B)+\beta_1 X_B\right] \quad m^2 mole/Js$$

$$\beta_1 = 1 \text{ or } 0.5; \quad \beta_2 = 0.5 \text{ or } 1$$

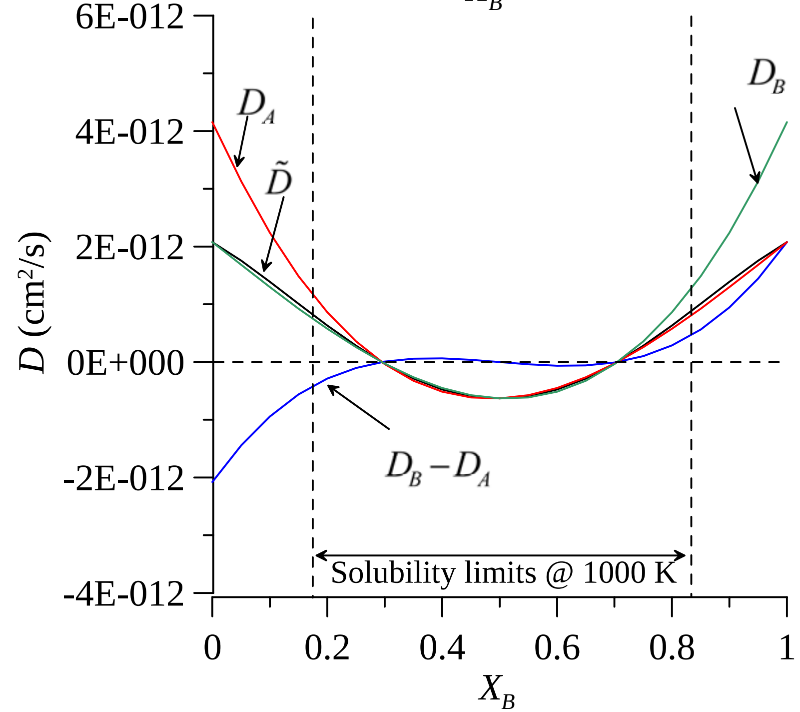
$$\Omega = 2*10^4 \quad J/mole$$

$$\frac{K}{\Omega} = 10^{-4} \quad m$$

$$R = 8.314 \quad J/moleK$$

$$T = 10^3 K$$

$$M_0 RT = 4.157\text{x}10^{-12} \text{ m}^2/\text{s}$$

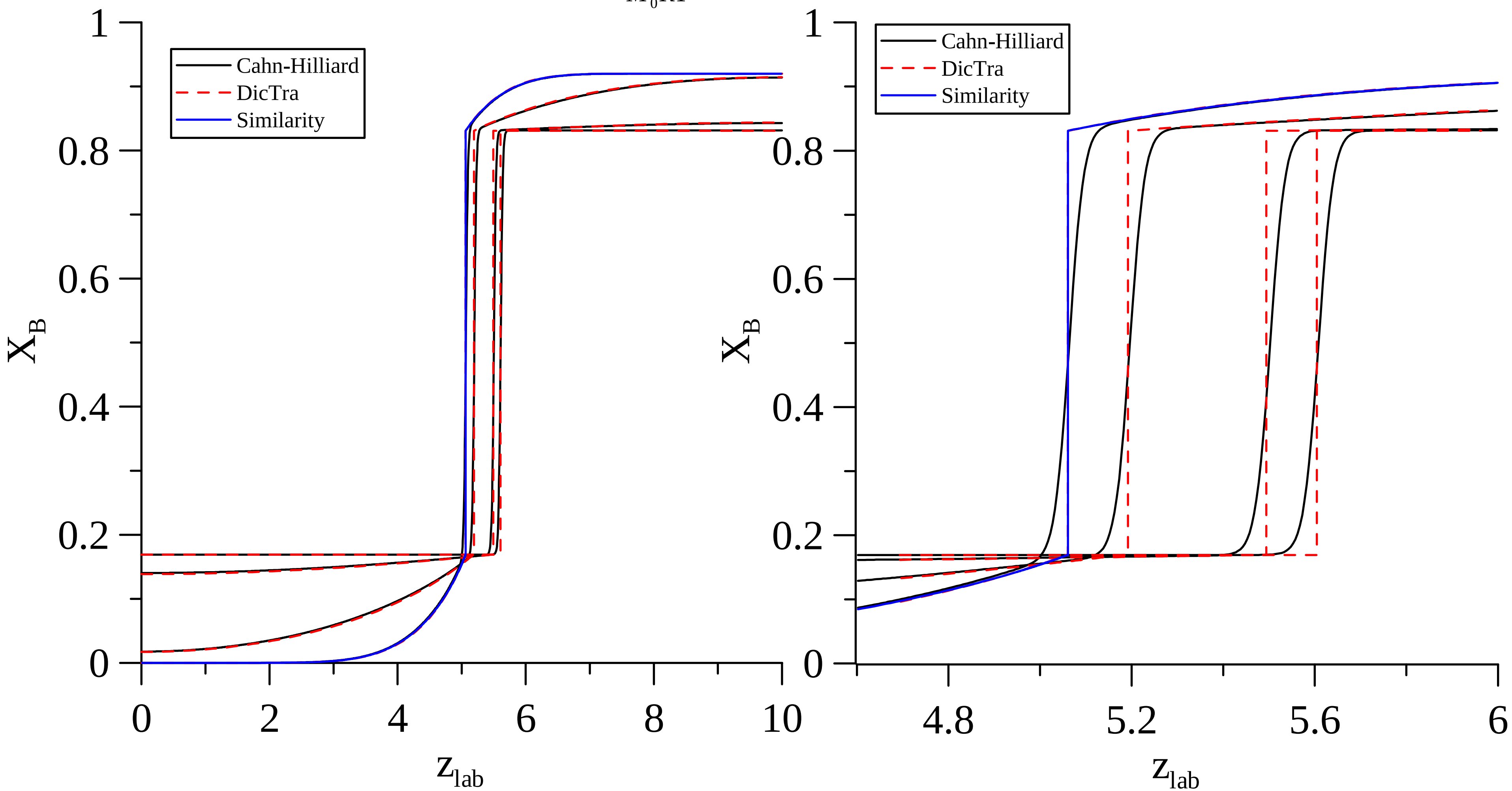


Comparison of Similarity Solution, DICTRA and Cahn-Hilliard Concentration

$X_B(-\infty,0) = 0$, $X_B(+\infty,0) = 0.92$

$(\beta_1 = 1, \beta_2 = 0.5)$

$t = 10^{-4},\ 10^{-3},\ 10^{-2},\ 10^{-1}$ in time units of $\dfrac{L^2}{M_0 RT}$

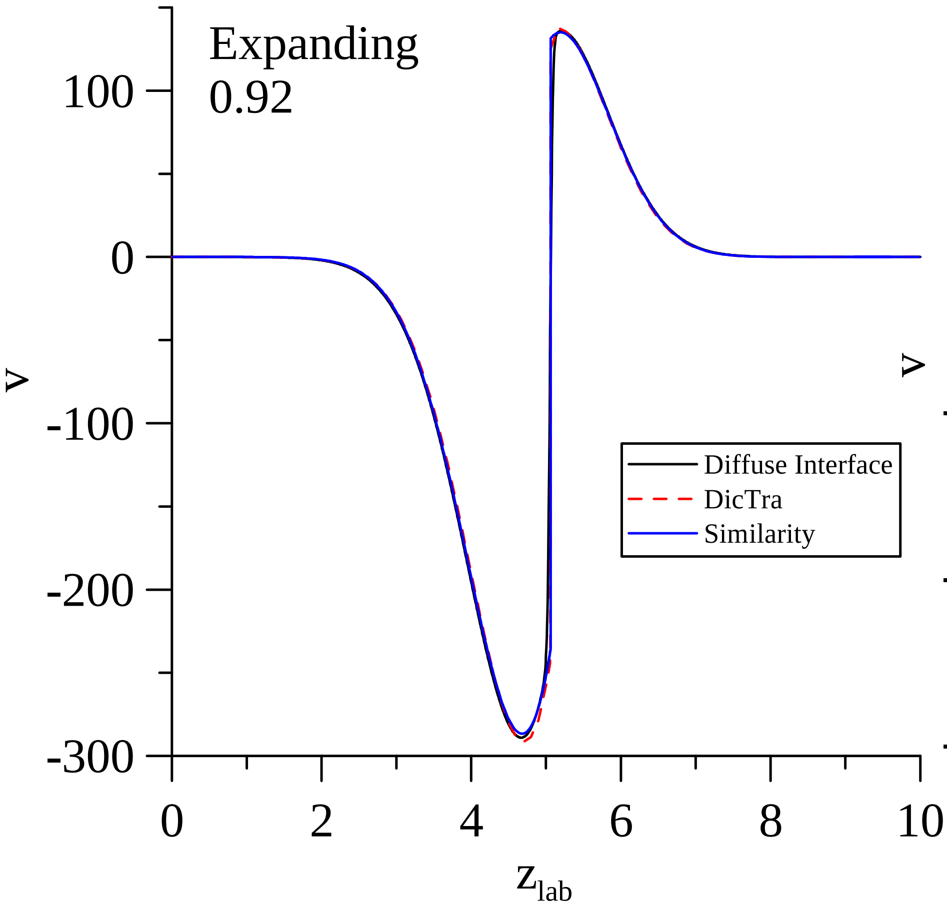


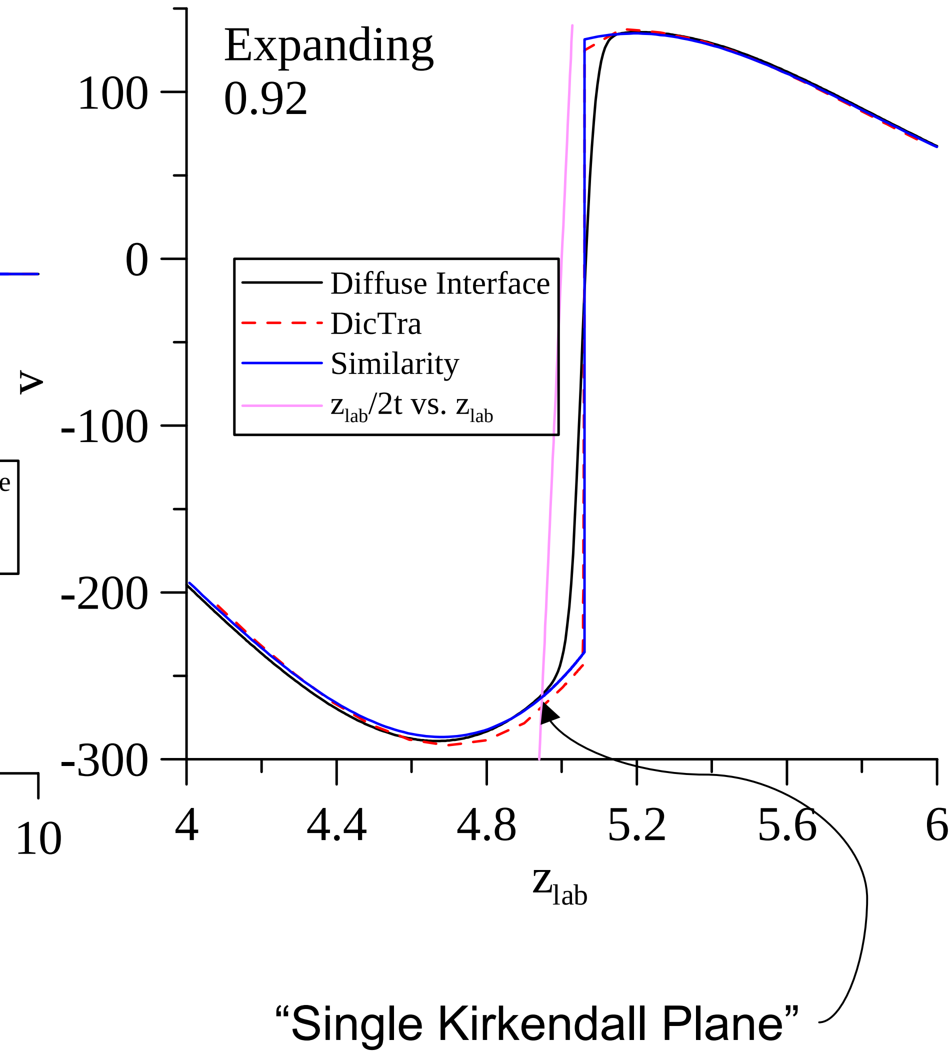
z / L

Box is 10**L**

Comparison of Similarity Solution, DICTRA and Diffuse Model
Marker Velocity

$X_B(-\infty,0) = 0$, $X_B(+\infty,0) = 0.92$
$(\beta_1 = 1, \beta_2 = 0.5)$

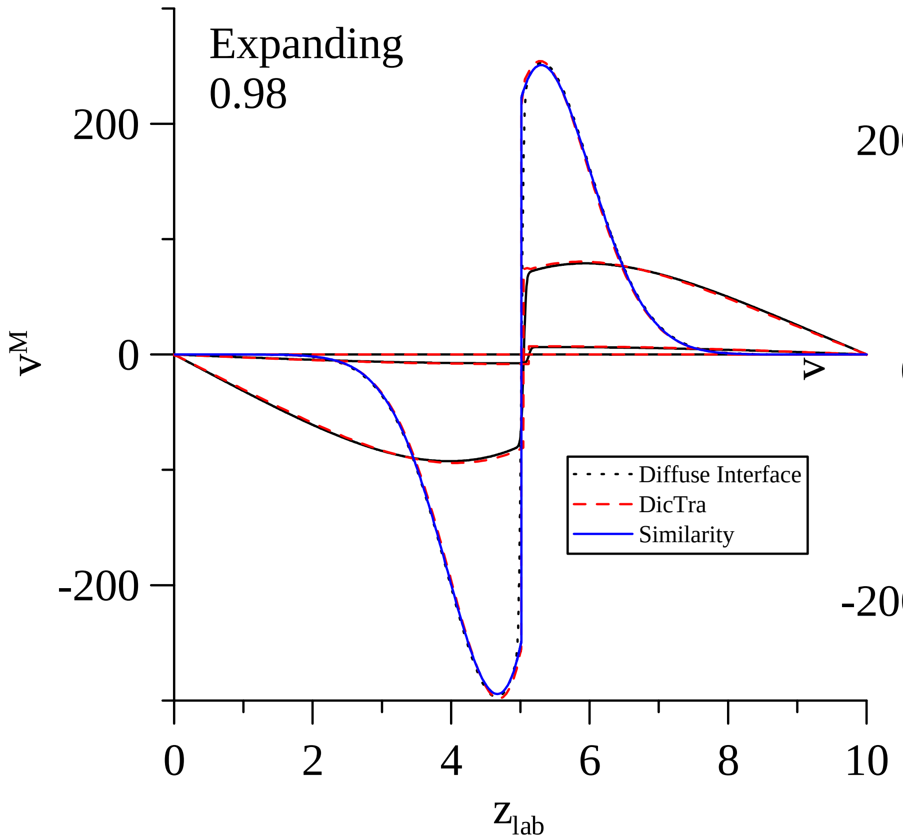


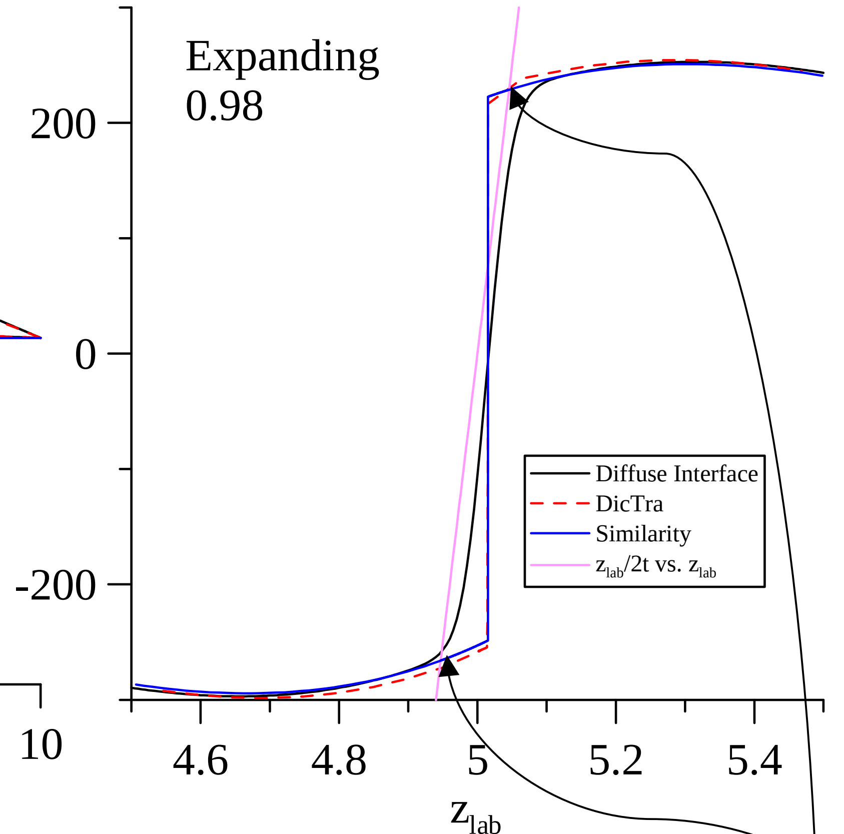


Slightly Different Right End Composition

$X_B(-\infty,0) = 0,\ X_B(+\infty,0) = 0.98$

$(\beta_1 = 1,\ \beta_2 = 0.5)$

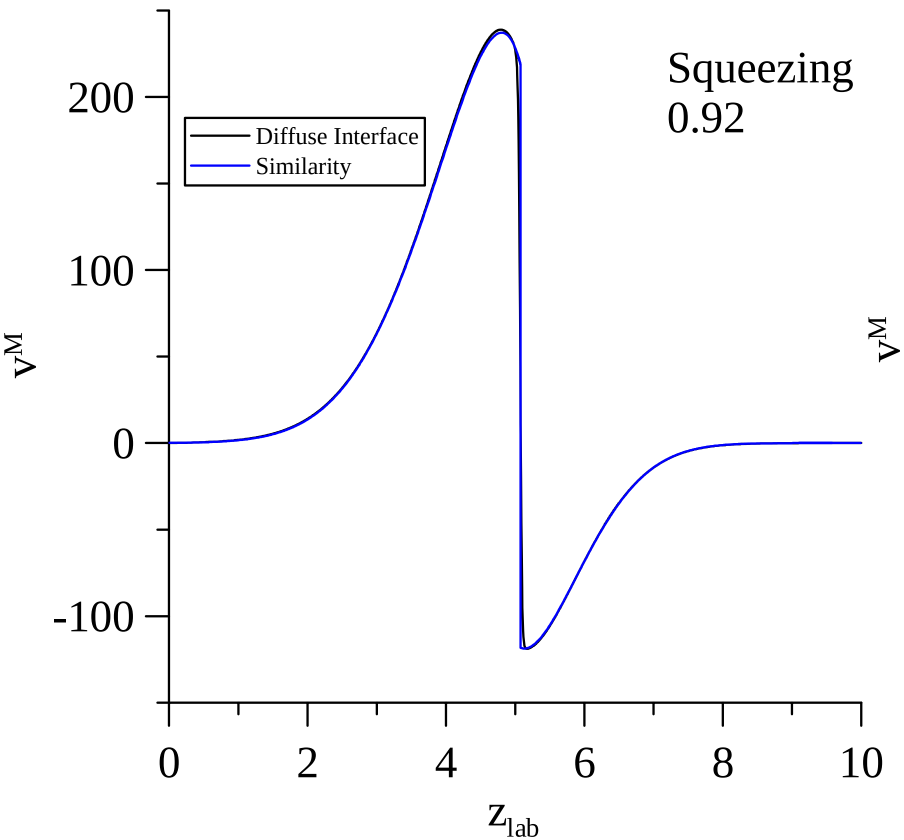


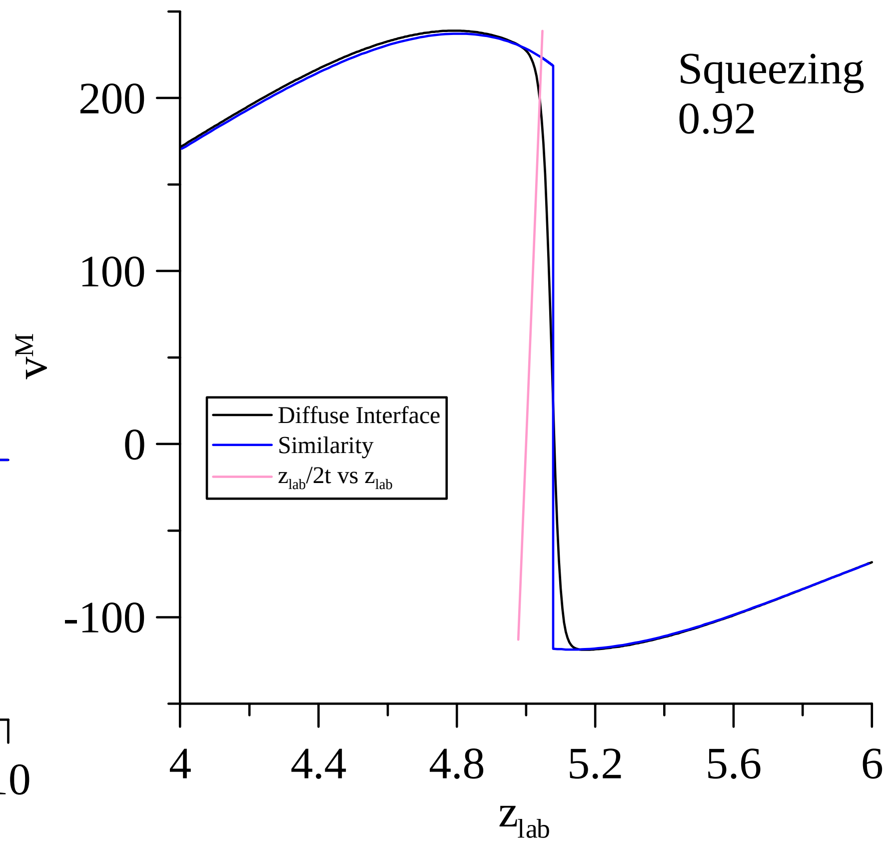


"Two Kirkendall Planes"

$X_B(-\infty,0) = 0$, $X_B(+\infty,0) = 0.98$

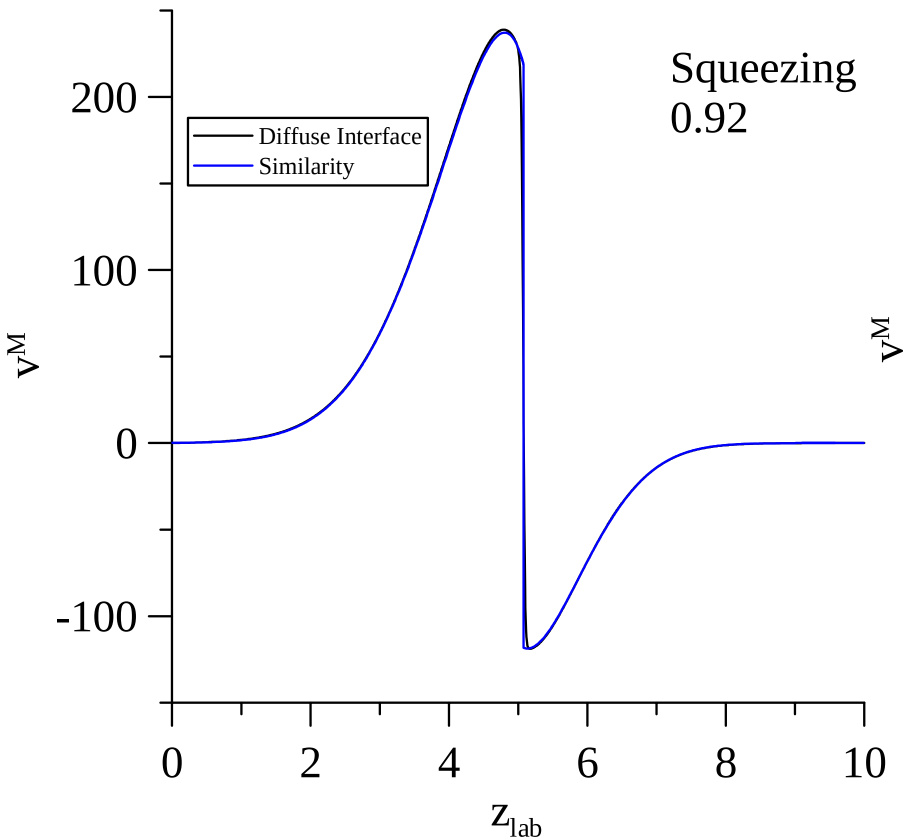
($\beta_1 = 1$, $\beta_2 = 0.5$)

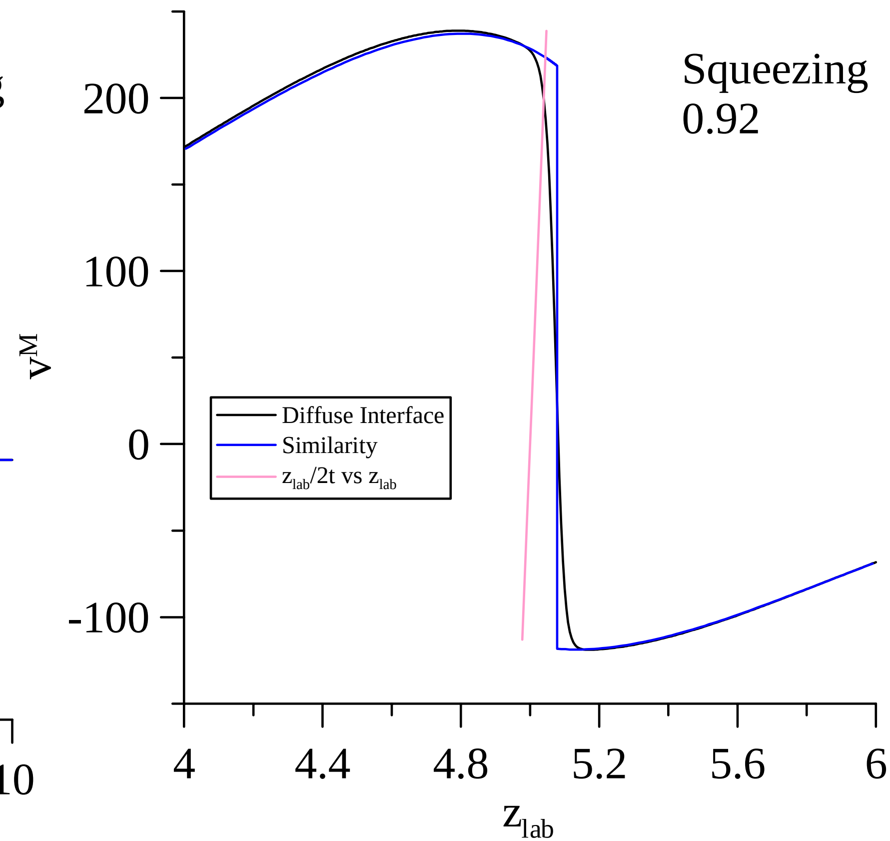




$X_B(-\infty,0) = 0$, $X_B(+\infty,0) = 0.98$

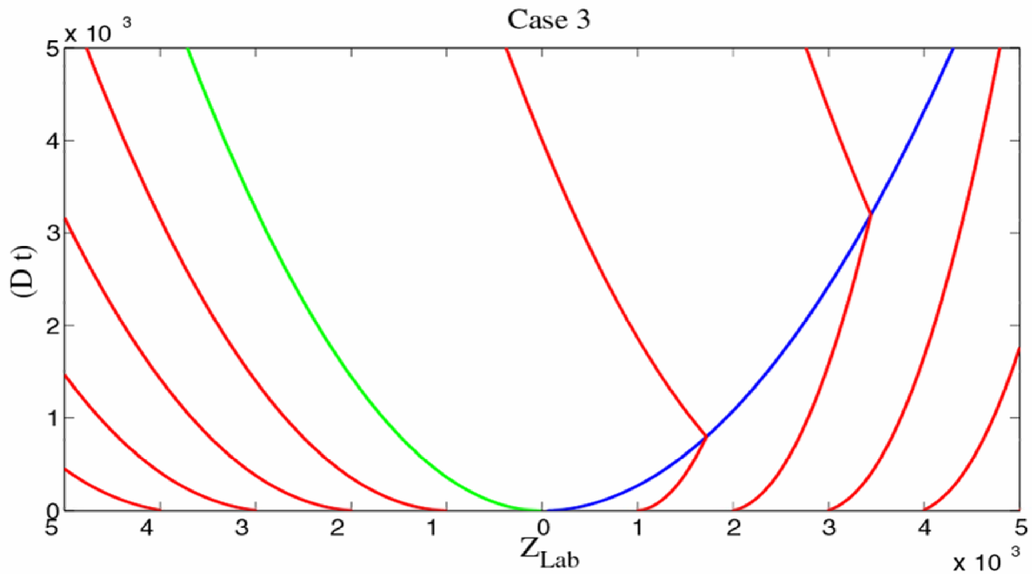
($\beta_1 = 1$, $\beta_2 = 0.5$)



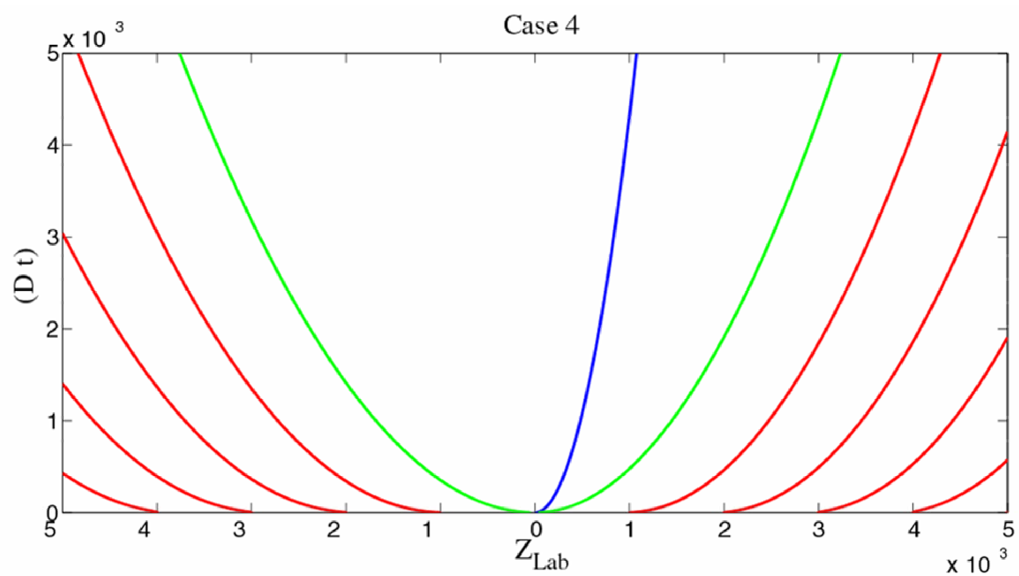


Similarity Solution: Expanding

0.92



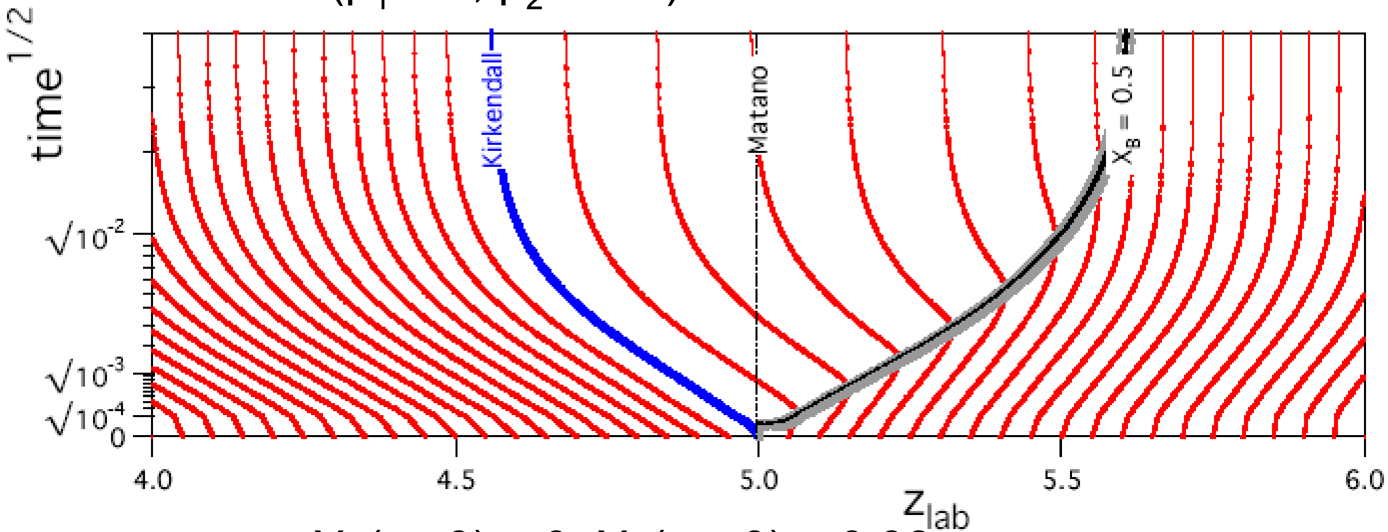
0.98



Expanding

$X_B(-\infty,0) = 0,\ X_B(+\infty,0) = 0.92$

$(\beta_1 = 1,\ \beta_2 = 0.5)$



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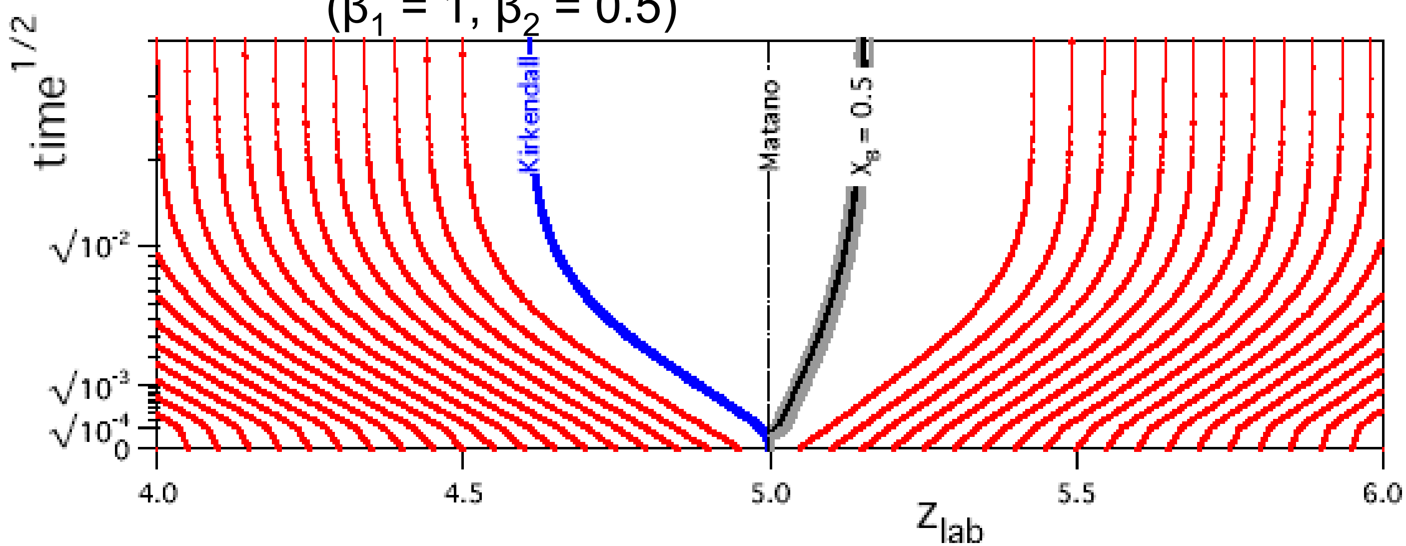

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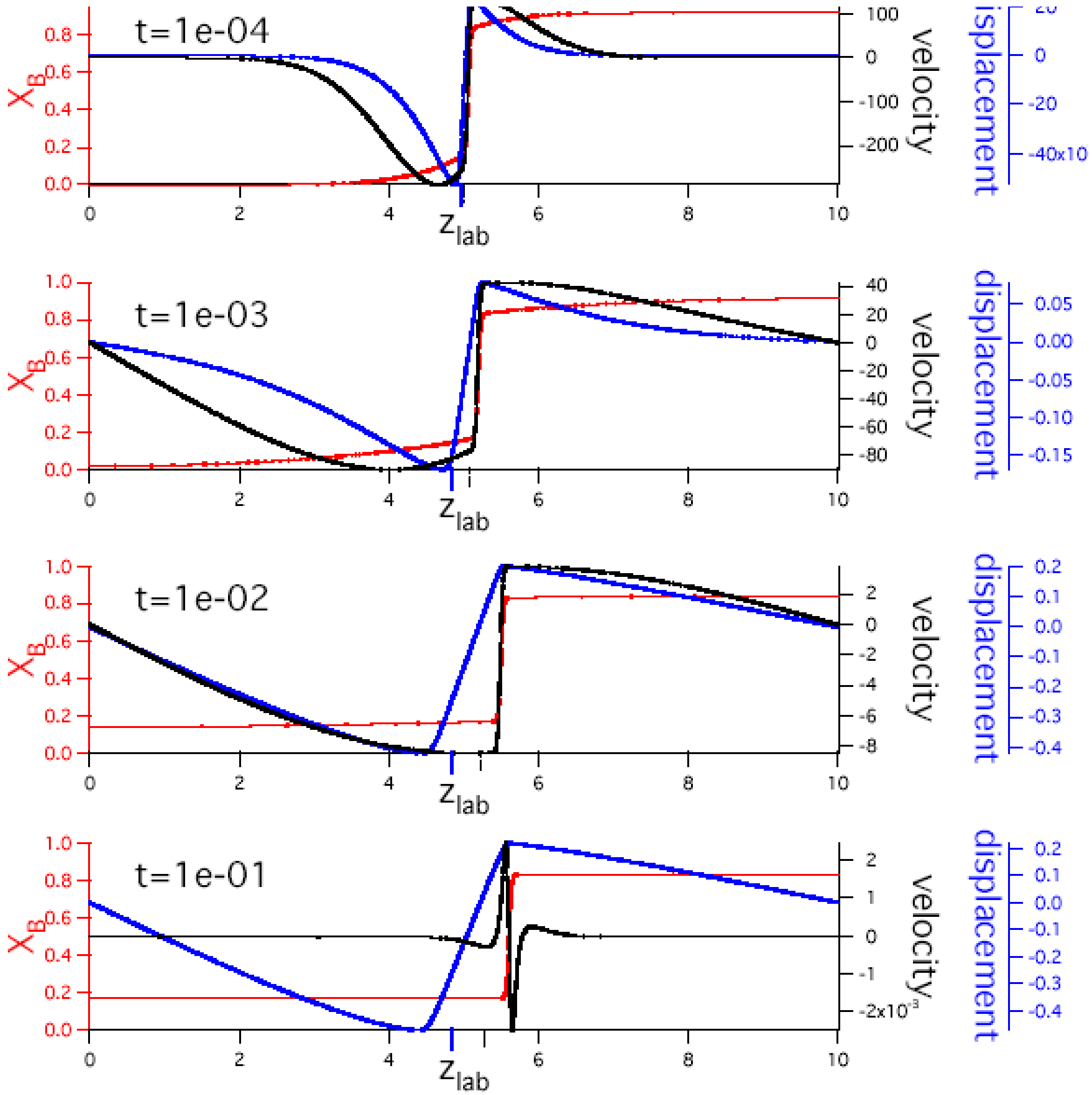
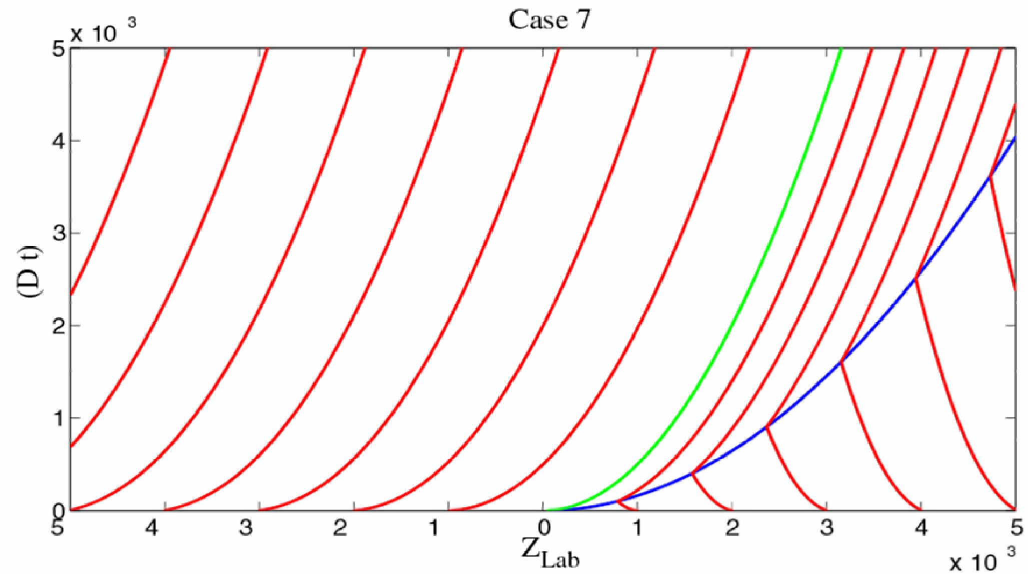
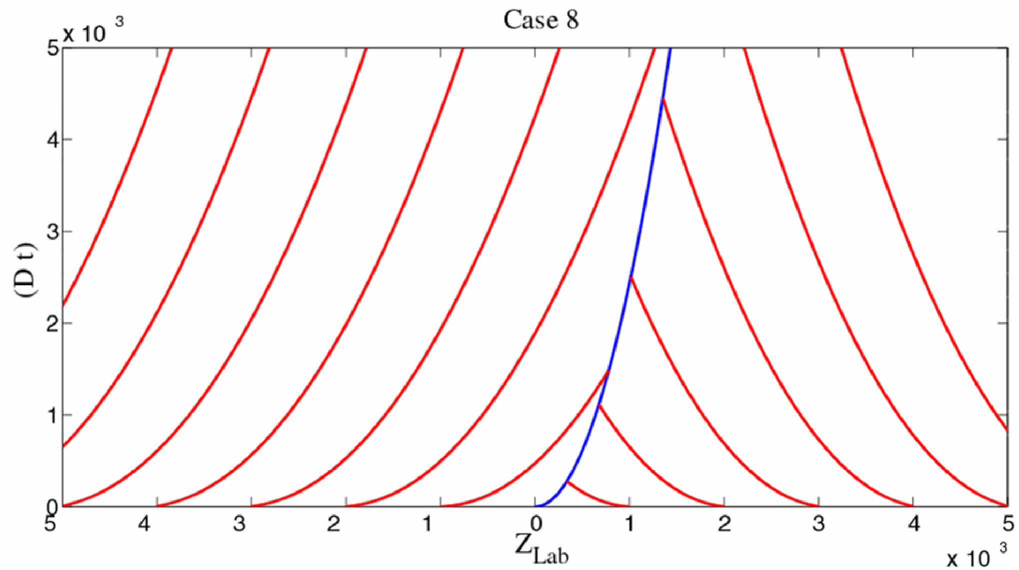


Similarity Solution: Squeezing

0.92



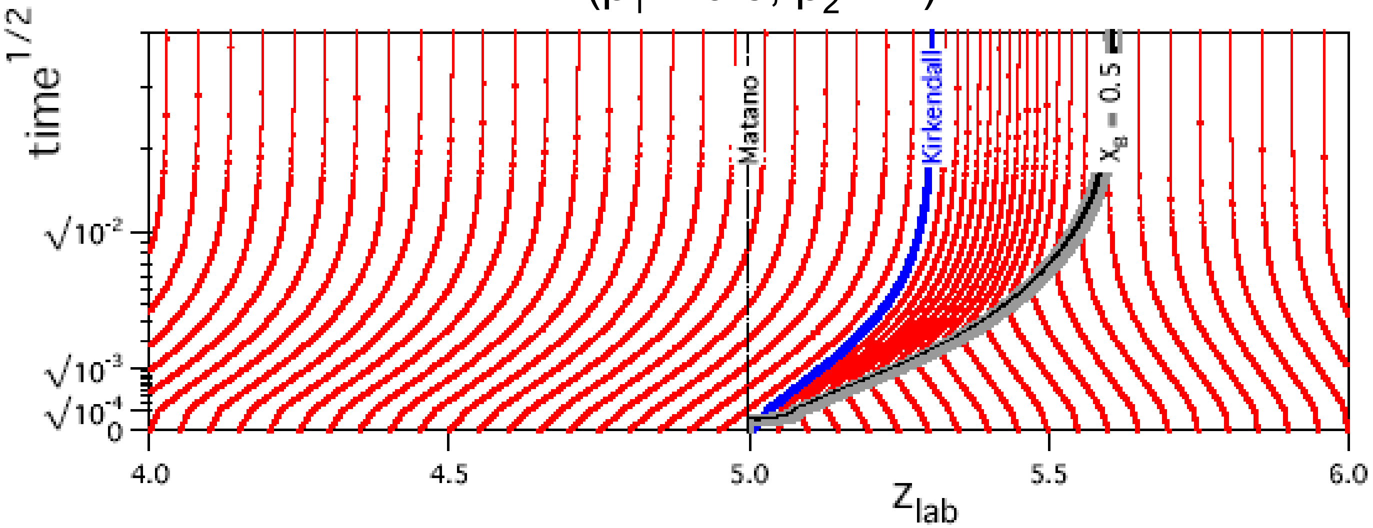
0.98



Squeezing

$X_B(-\infty,0) = 0$, $X\ (-\infty,X_B(+\infty,0) = 0.92$

$(\beta_1 = 0.5,\ \beta_2 = 1)$



$X_B(-\infty,0) = 0$, $X_B(+\infty,0) = 0.98$

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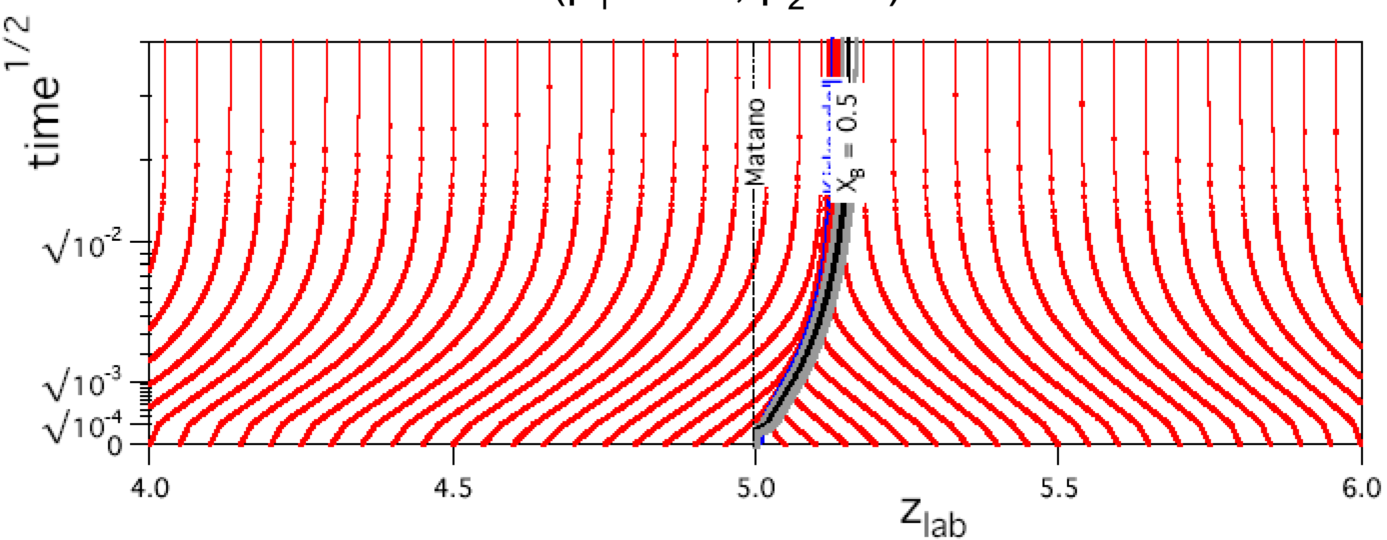

$X_B(-\infty,0) = 0$, $(X_B(+\infty,0) = 0.98$

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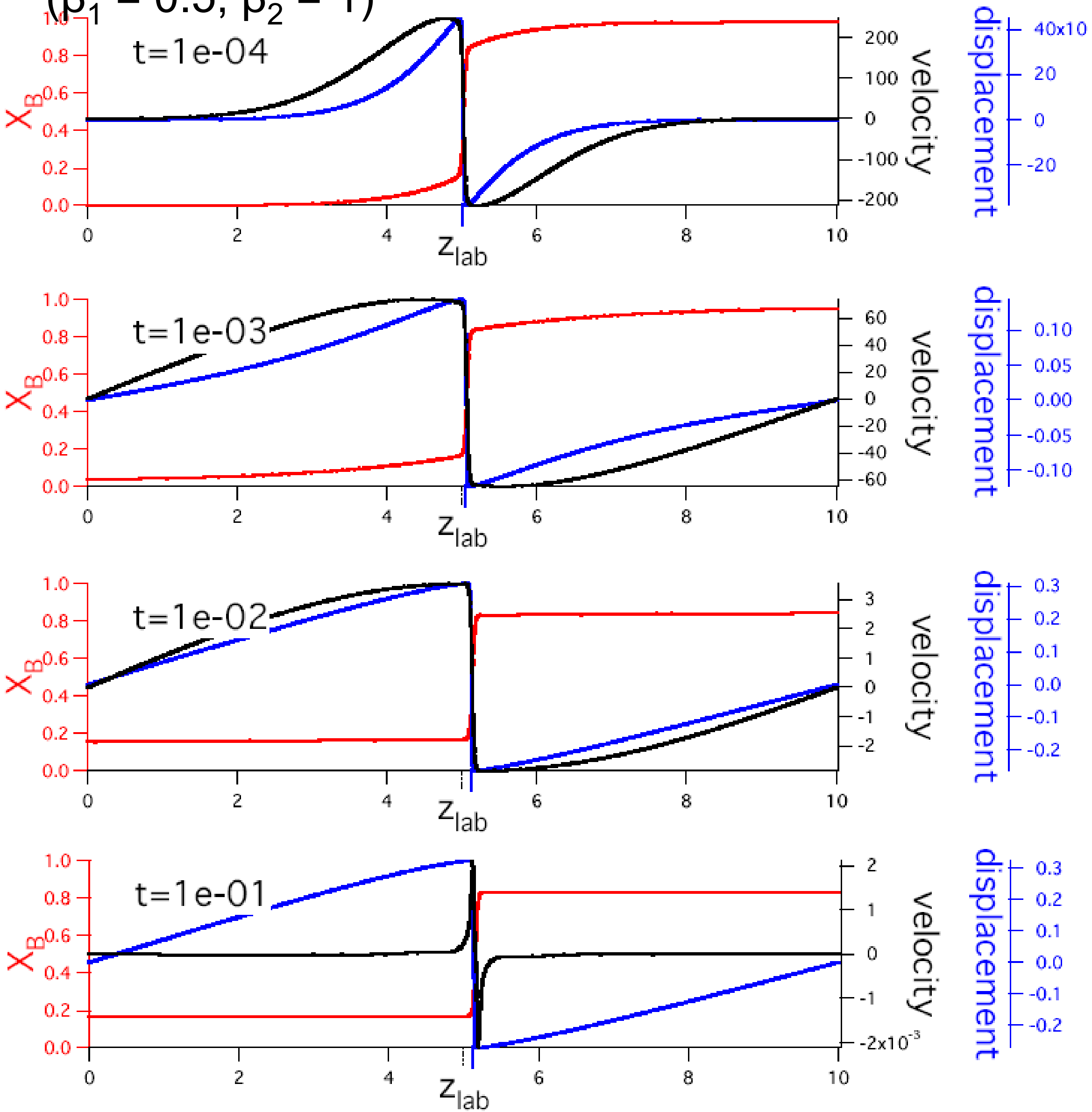
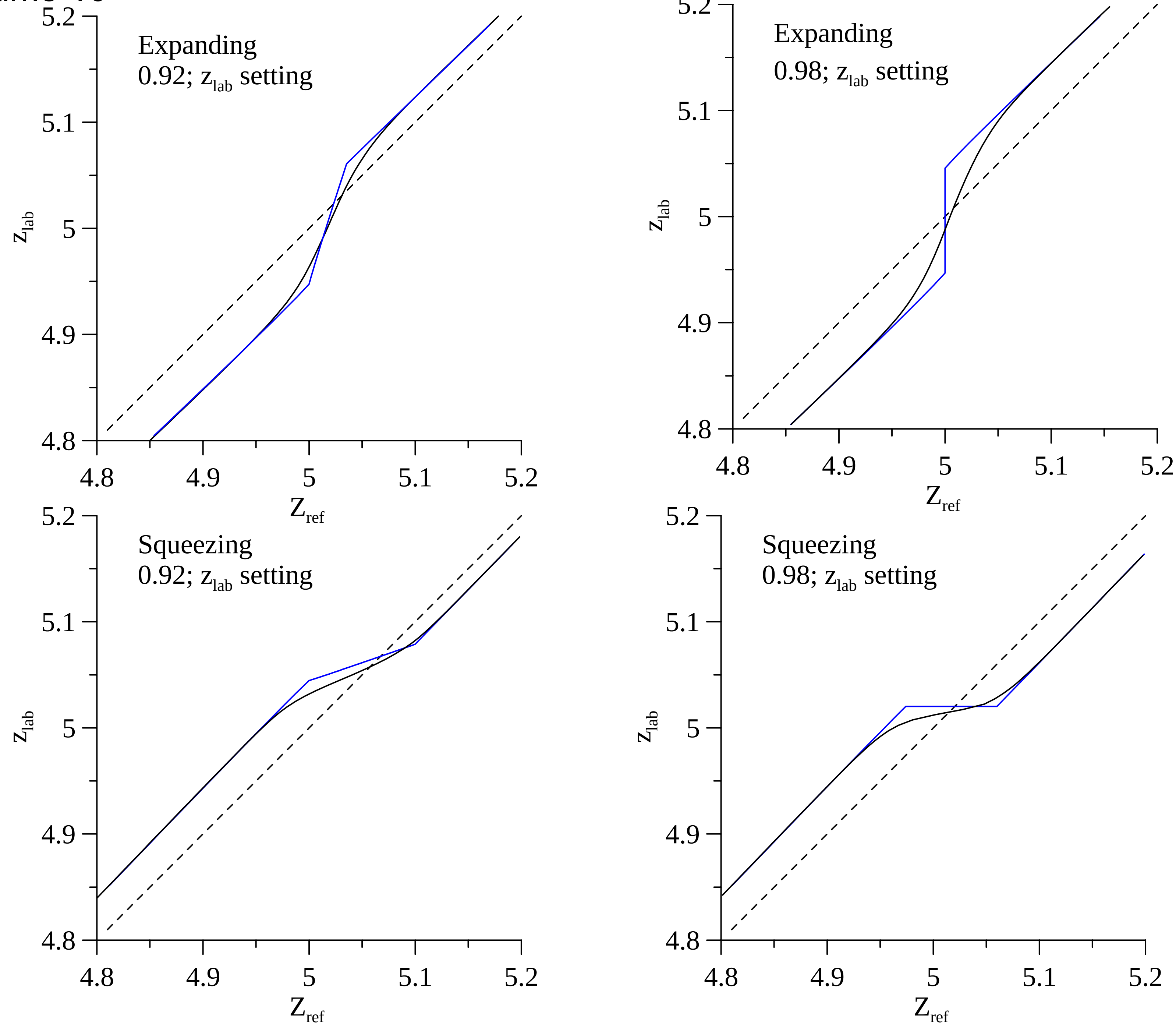


Fixed time 10^{-4}



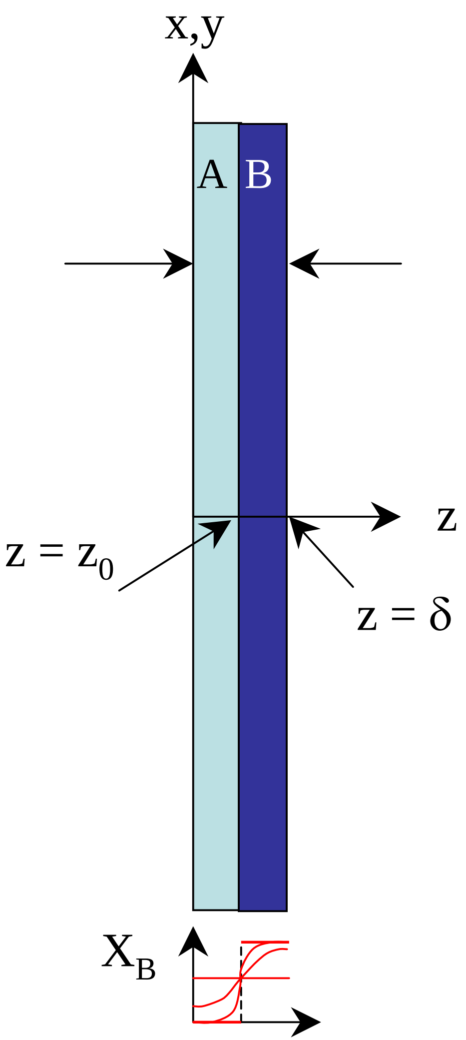
Simple free beam model; Two phase

Curvature, $\kappa(t)$

Neutral axis position @ $z = c(t)$

$$\sigma_{zz} = 0$$

$$\varepsilon_{xx}^{T}(z,t) = \varepsilon_{yy}^{T}(z,t) = \kappa(t)\left(z - c(t)\right)$$



Balance of Forces, Balance of Moments

$$\begin{cases} 0 = \int_0^\delta \sigma_{xx} dz = \int_0^\delta E'\left(\varepsilon_{xx}^{T} - \varepsilon_{xx}^{0}\right) dz \\ 0 = \int_0^\delta z\sigma_{xx} dz = \int_0^\delta zE'\left(\varepsilon_{xx}^{T} - \varepsilon_{xx}^{0}\right) dz \end{cases}$$

Take $\dfrac{\partial}{\partial t}$

$$\begin{cases} 0 = \dfrac{\partial}{\partial t}\int_0^\delta \left[\left[\kappa(t)\left(z - c(t)\right)\right] dz\right] dz - \int_0^{z^*(t)} \dot{\varepsilon}_{xx}^{0\alpha} dz - \int_{z^*(t)}^{\delta} \dot{\varepsilon}_{xx}^{0\beta} dz \\ 0 = \dfrac{\partial}{\partial t}\int_0^\delta z\left[\kappa(t)\left(z - c(t)\right)\right] dz - \int_0^{z^*(t)} z\dot{\varepsilon}_{xx}^{0\alpha} dz - \int_{z^*(t)}^{\delta} z\dot{\varepsilon}_{xx}^{0\beta} dz \end{cases}$$

$$\dot{\varepsilon}_{xx}^{0\alpha} = -\frac{\Delta D^\alpha}{3}\frac{\partial^2 X_2^\alpha}{\partial z^2} = -\frac{\Delta D^\alpha}{3\tilde{D}^\alpha}\frac{\partial X_2^\alpha}{\partial t}; \quad 0 \le z \le z^*(t)$$

$$\dot{\varepsilon}_{xx}^{0\beta} = -\frac{\Delta D^\beta}{3}\frac{\partial^2 X_2^\beta}{\partial z^2} = -\frac{\Delta D^\beta}{3\tilde{D}^\beta}\frac{\partial X_2^\beta}{\partial t}; \quad z^*(t) \le z \le \delta$$

Integrating both wrt to t (& taking care of time dependent limits of intergation)

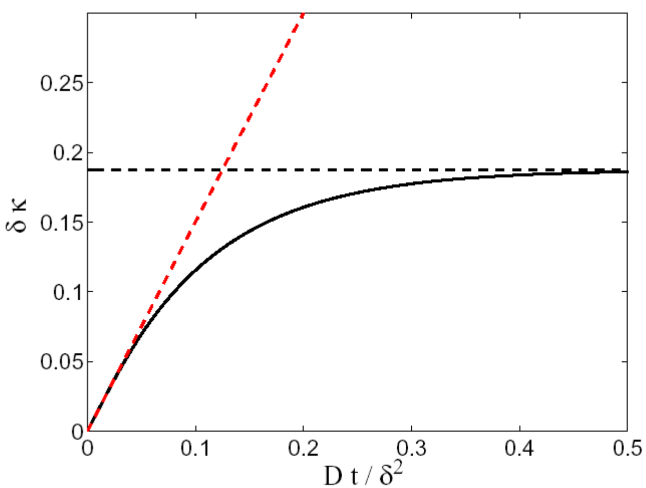
$$
\begin{cases}
0=\int_0^{\delta}\left[\kappa(t)\left(z-c(t)\right)\right]dz+\dfrac{\Delta D^{\alpha}}{3\tilde{D}^{\alpha}}\left\{-\left(z^*(t)-z_0\right)X_2^{\alpha\beta}+\int_0^{z^*(t)}\left[X_2^{\alpha}(z,t)-X_2^{\alpha}(z,0)\right]dz\right\} \\
\qquad +\dfrac{\Delta D^{\beta}}{3\tilde{D}^{\beta}}\left\{\left(z^*(t)-z_0\right)X_2^{\beta\alpha}+\int_{z^*(t)}^{\delta}\left[X_2^{\beta}(z,t)-X_2^{\beta}(z,0)\right]dz\right\} \\
0=\int_0^{\delta}z\left[\kappa(t)\left(z-c(t)\right)\right]dz+\dfrac{\Delta D^{\alpha}}{3\tilde{D}^{\alpha}}\left\{-\left(z^{*2}(t)-z_0^2\right)X_2^{\alpha\beta}+\int_0^{z^*(t)}z\left[X_2^{\alpha}(z,t)-X_2^{\alpha}(z,0)\right]dz\right\} \\
\qquad +\dfrac{\Delta D^{\beta}}{3\tilde{D}^{\beta}}\left\{\left(z^{*2}(t)-z_0^2\right)X_2^{\beta\alpha}+\int_{z^*(t)}^{\delta}z\left[X_2^{\beta}(z,t)-X_2^{\beta}(z,0)\right]dz\right\}
\end{cases}
$$

For single phase problem

can solve diffusion problem by Fourrier methods

e.g., $z_0=\delta/2,\ z^*(t)=\delta/2$ Get

$$
\begin{cases} c(t)=\delta/2 \\ \kappa(t) \end{cases}
$$



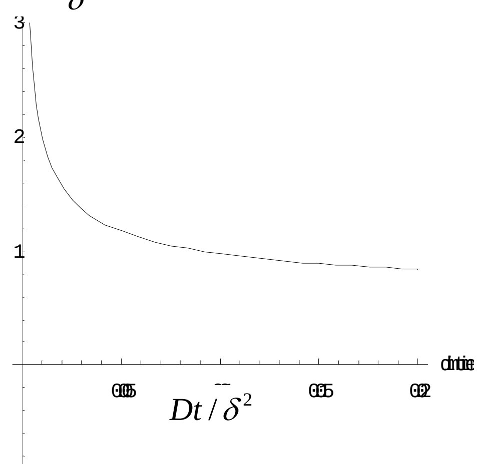
For two phase problem

can use error function solution for moving interface if $t \ll \dfrac{\delta^2}{\tilde{D}}$

$z^*(t)=K\sqrt{4\tilde{D}^{\beta}t}$ & etc.

$$
\begin{cases} c(t) \\ \kappa(t) \end{cases}
$$

$\alpha(t)=\dfrac{c(t)}{\delta}$



$\delta K(t)$