Transient Interfacial Phenomena in Miscible Polymer Systems
(TIPMPS)

A flight project in the Microgravity Materials Science Program

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What is the question to be answered?

Can gradients of composition and temperature in miscible polymer/monomer systems create stresses that cause convection?

Why?

The objective of TIPMPS is to confirm Korteweg’s model that stresses could be induced in miscible fluids by concentration gradients, causing phenomena that would appear to be the same as with immiscible fluids. The existence of this phenomenon in miscible fluids will open up a new area of study for materials science.

Many polymer processes involving miscible monomer and polymer systems could be affected by fluid flow and so this work could help understand miscible polymer processing, not only in microgravity, but also on earth.

How

An interface between two miscible fluids will be be created by photopolymerization, which allows the creation of precise and accurate concentration gradients between polymer and monomer.

Optical techniques will be used to measure the refractive index variation caused by the resultant temperature and concentration fields.

Impact

Demonstrating the existence of this phenomenon in miscible fluids will open up a new area of study for materials science.

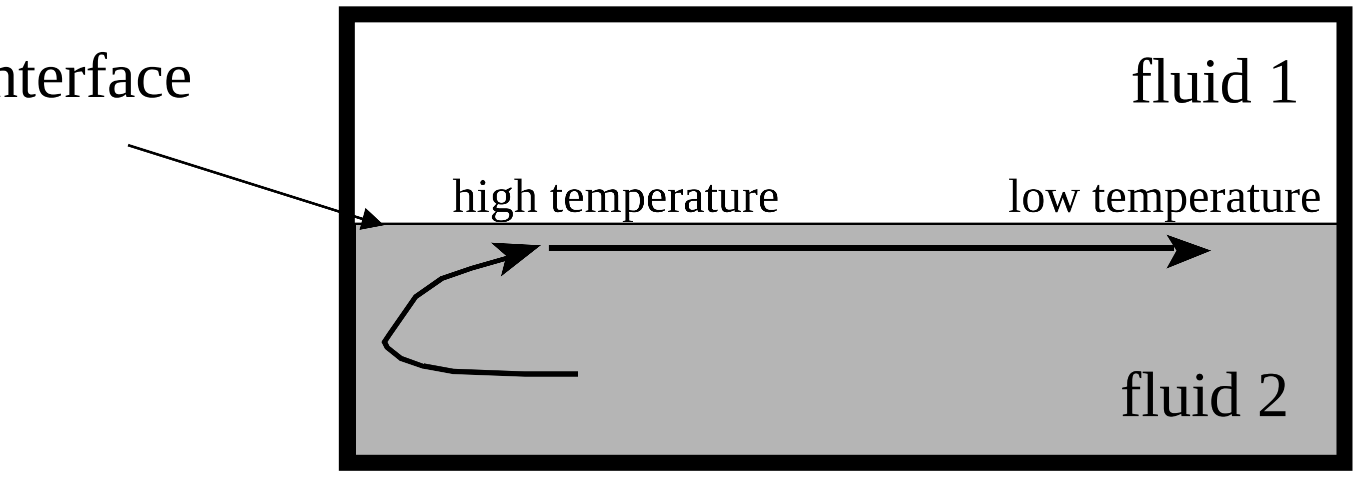
> “If gradients of composition and temperature in miscible polymer/monomer systems create stresses that cause convection then it would strongly suggest that stress-induced flows could occur in many applications with miscible materials. The results of this investigation could then have potential implications in *polymer blending (phase separation), colloidal formation, fiber spinning, polymerization kinetics, membrane formation and polymer processing in space.*”
>
> SCR Panel, December 2000.

Science Objectives

- **Determine if convection can be induced by variation of the width of a miscible interface**
- **Determine if convection can be induced by variation of temperature along a miscible interface**
- **Determine if convection can be induced by variation of conversion along a miscible interface**

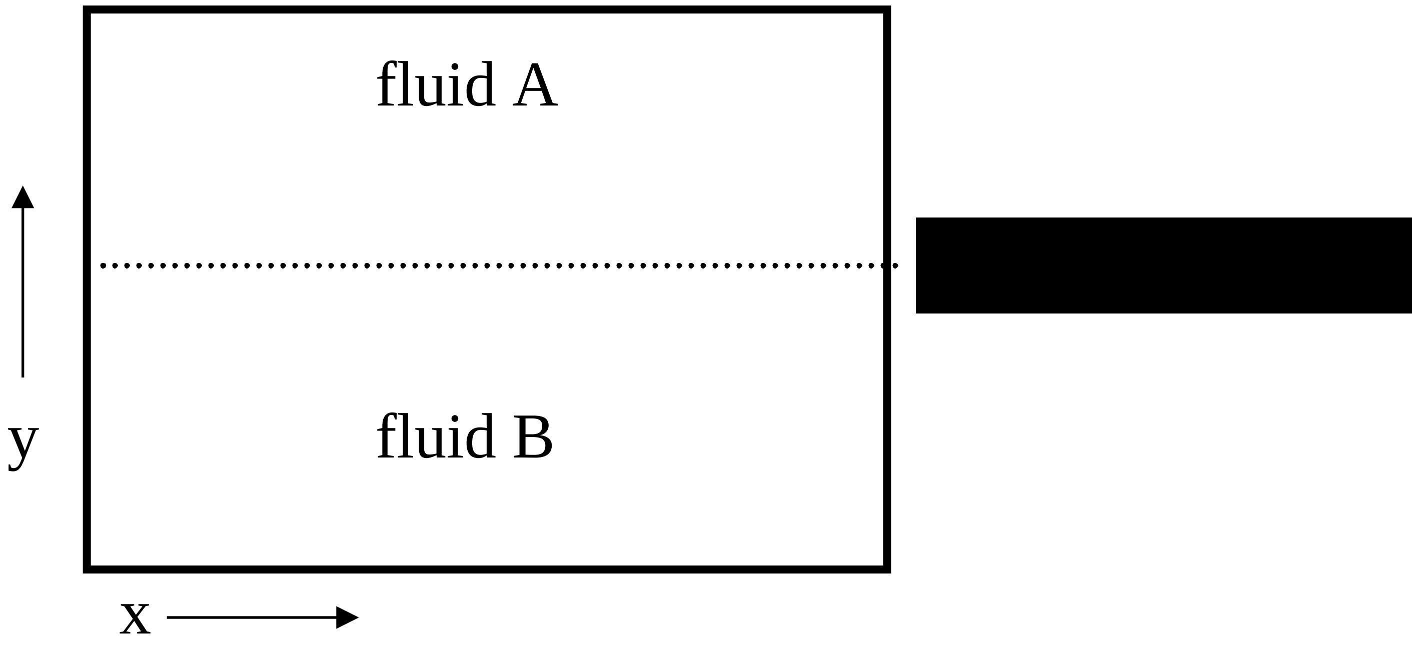
Surface-Tension-Induced Convection

convection caused by gradients in surface (interfacial) tension between immiscible fluids, resulting from gradients in concentration and/or temperature

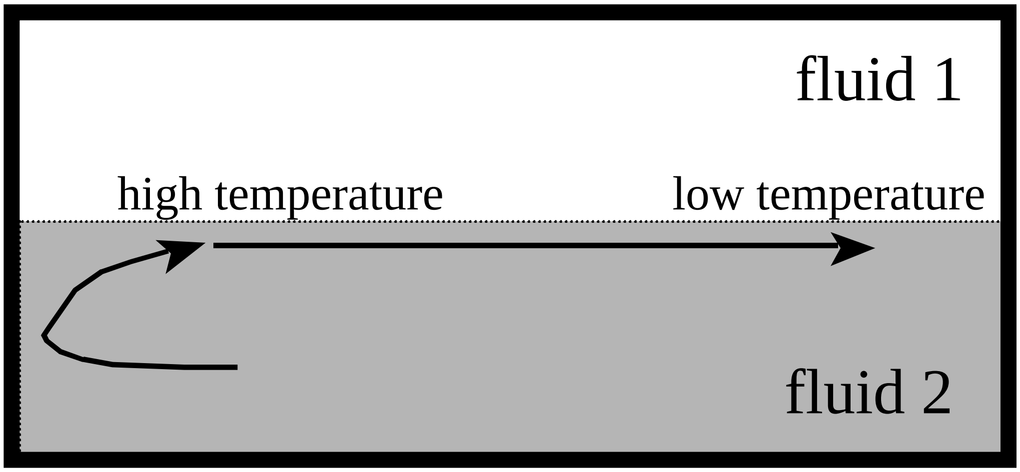


Consider a Miscible “Interface”

C = volume fraction of A



Can the analogous process occur with miscible fluids?

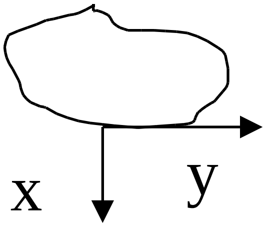


Korteweg (1901)

- treated liquid/vapor interface as a continuum
- used Navier-Stokes equations plus tensor depending on density derivatives
- for miscible liquid, diffusion is slow enough that “a provisional equilibrium” could exist (everything in equilibrium except diffusion)
  - i.e., no buoyancy
- fluids would act like immiscible fluids

Korteweg Stress

- mechanical interpretation (“tension”)



$$p_N - p_T = k\left(\frac{dc}{dx}\right)^2$$

k has units of N

$$\sigma = \int k\left(\frac{dc}{dx}\right)^2 dx$$

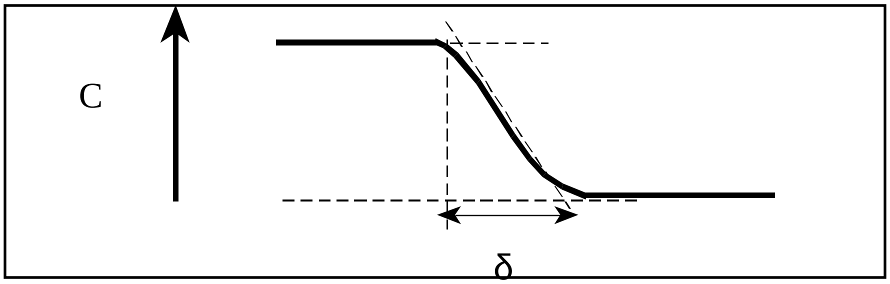
σ has units of N m

$$\frac{F}{V} = k\frac{\partial}{\partial y}\left(\frac{\partial c}{\partial x}\right)^2$$

Change in a concentration gradient along the interface causes a volume force

Hypothesis: Effective Interfacial Tension

$$\sigma = k\frac{(\Delta C)^2}{\delta}$$



k is the same parameter in the Korteweg model

(Derived by Zeldovich in 1949)

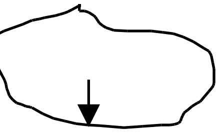
Theory of Cahn and Hilliard

Thermodynamic approach

Cahn, J. W.; Hilliard, J. E. "Free Energy of a Nonuniform System. I. Interfacial Free Energy," *J. Chem. Phys.* **1958**, *28,* 258-267**.**

$$\boxed{g = \int g_0 + k| \quad C|^2}$$

square gradient contribution to surface free energy (J m^{-2})



$$\sigma = k\int \quad {}^2C(r)dr$$

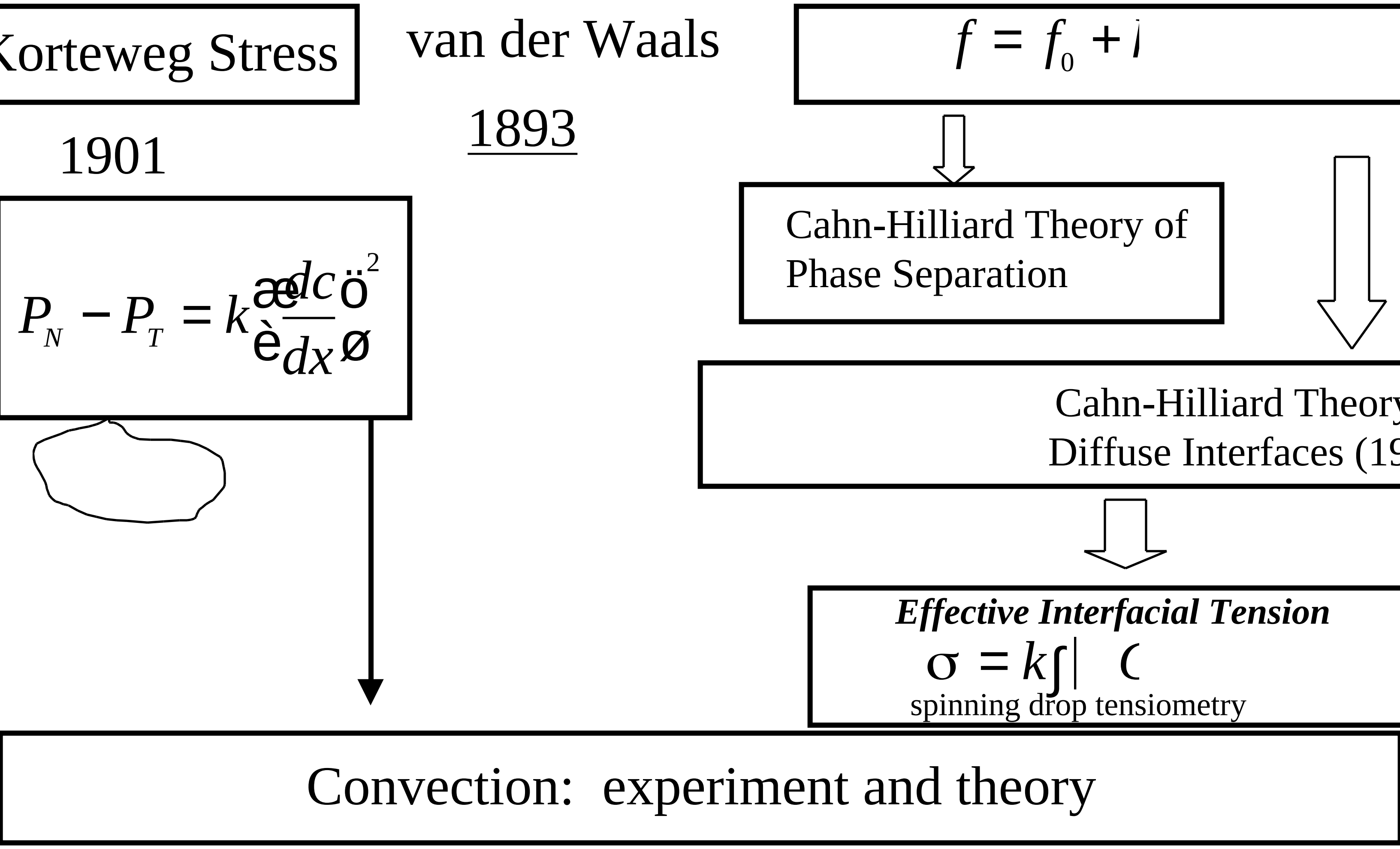
also called the surface tension (N m^{-1})

k > 0

Mechanics

Nonuniform Materials

Thermodynamic



Square gradient theory

Korteweg Stress

1901

van der Waals

1893

$f = f_0 +$

$$P_N - P_T = k\left(\frac{dc}{dx}\right)^2$$

Cahn-Hilliard Theory of
Phase Separation

Cahn-Hilliard Theory
Diffuse Interfaces (19

Effective Interfacial Tension

$\sigma = k\int|$

spinning drop tensiometry

Convection: experiment and theory

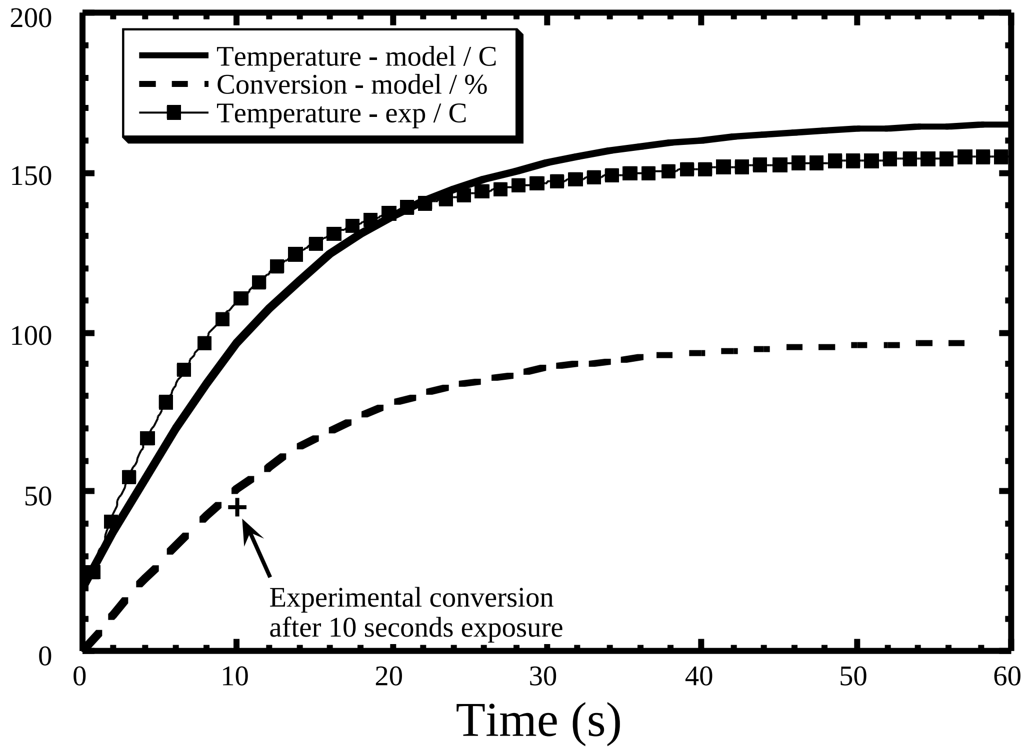
Why is this important?

- answer a 100 year-old question of Korteweg
- stress-induced flows could occur in many applications with miscible materials
- link mechanical theory of Korteweg to thermodynamic theory of Cahn & Hilliard
- test theories of polymer-solvent interactions

How?

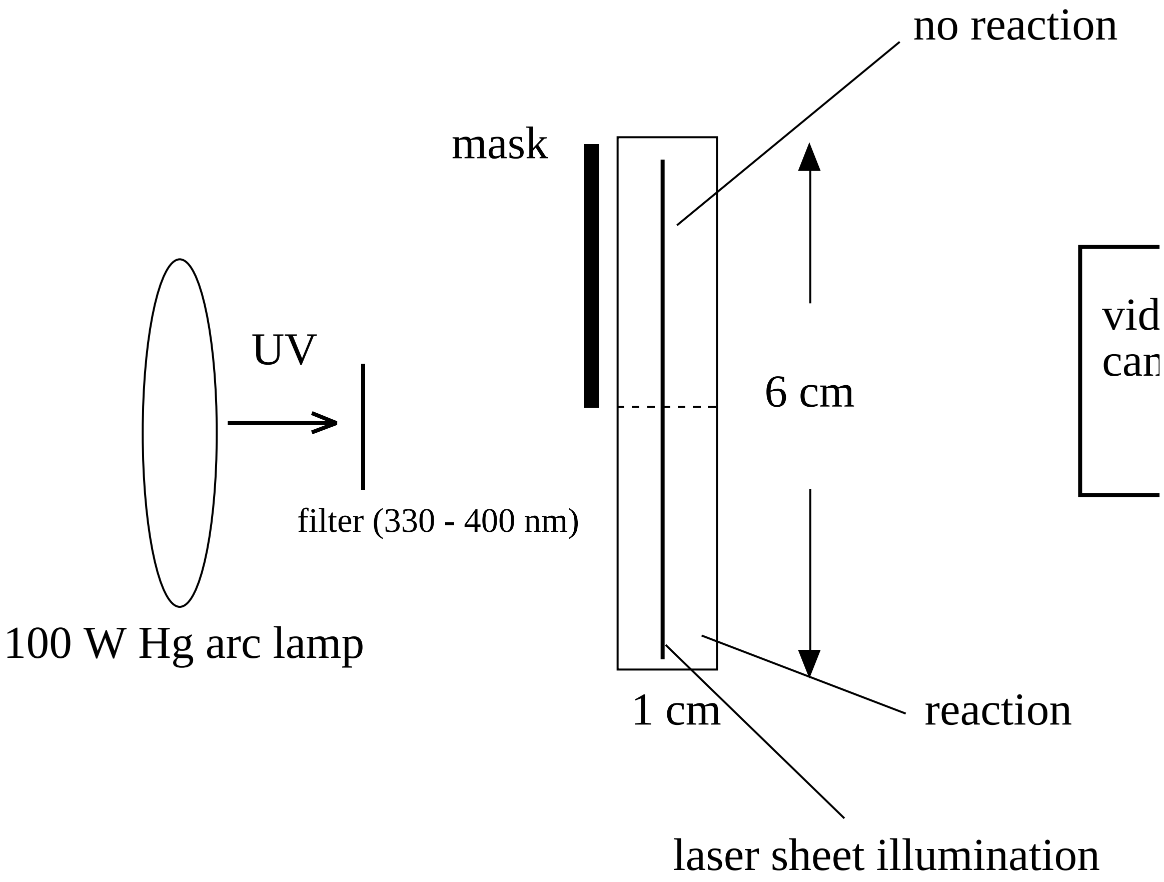
- photopolymerization of dodecyl acrylate
- masks to create concentration gradients
- measure fluid flow by PIV or PTV
- use change in fluorescence of pyrene to measure viscosity

Photopolymerization can be used to rapidly prepare polymer/monomer interfaces



We have an excellent model to predict reaction rates and conversion

Schematic


no reaction

mask

UV

vid
can

6 cm

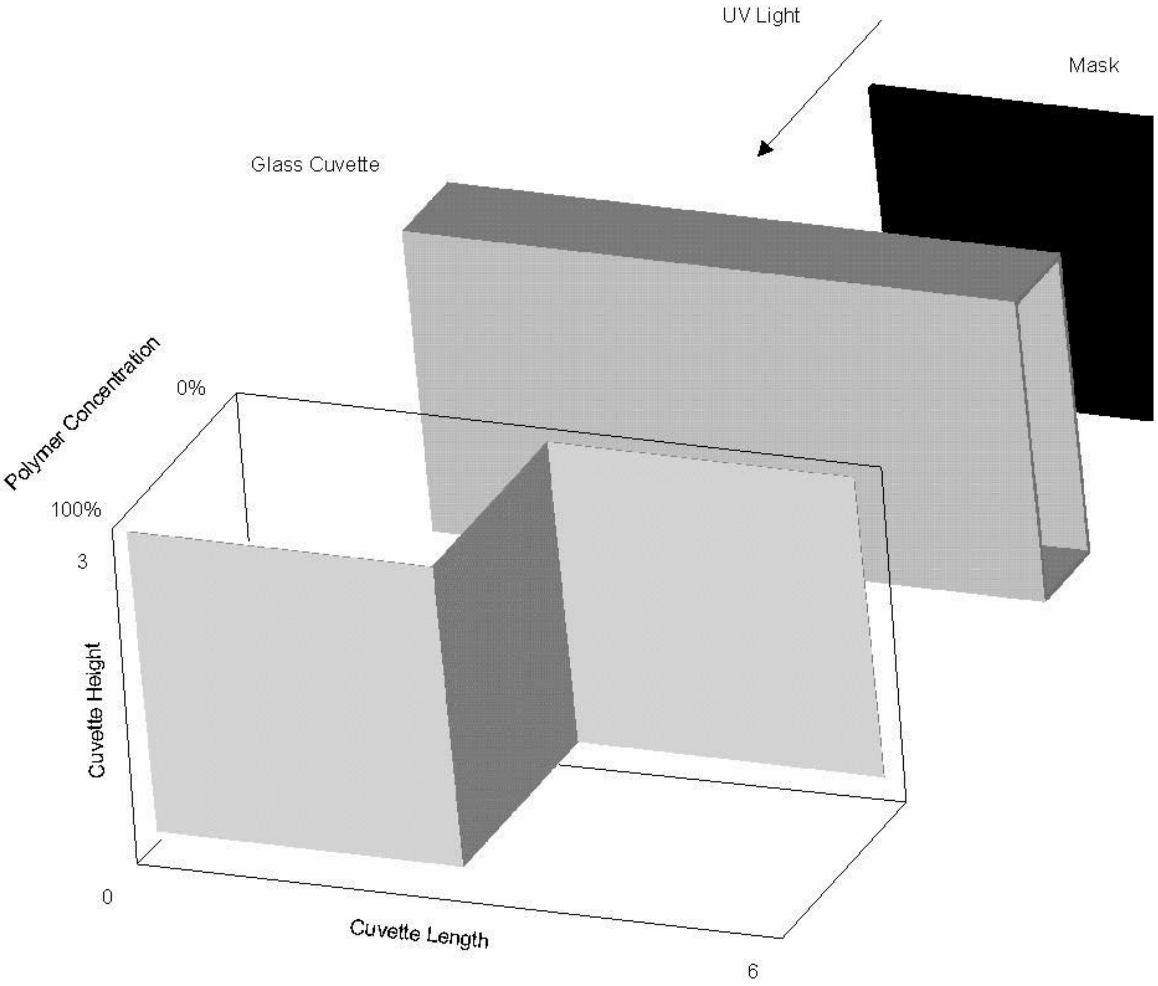
filter (330 - 400 nm)

100 W Hg arc lamp

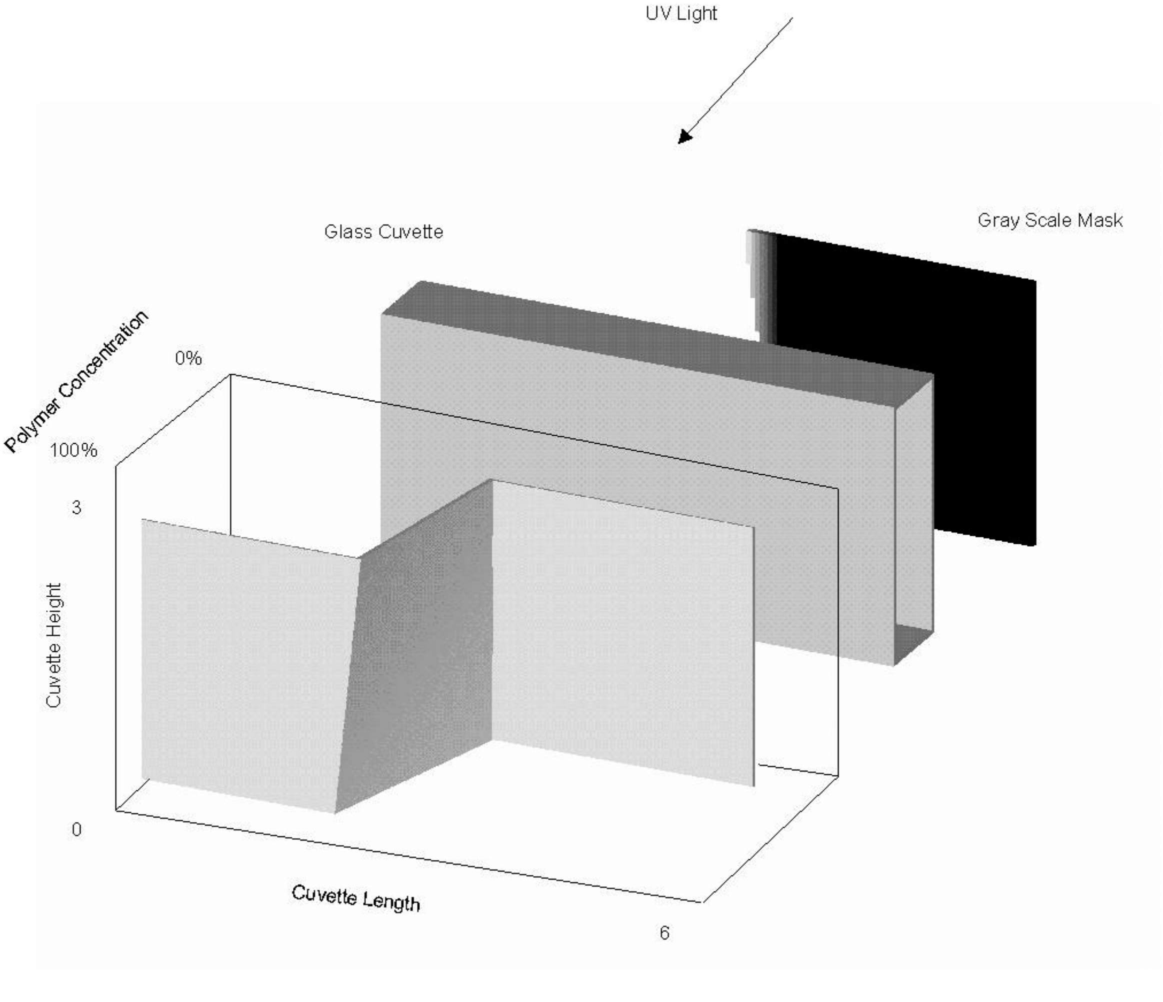
1 cm

reaction

laser sheet illumination

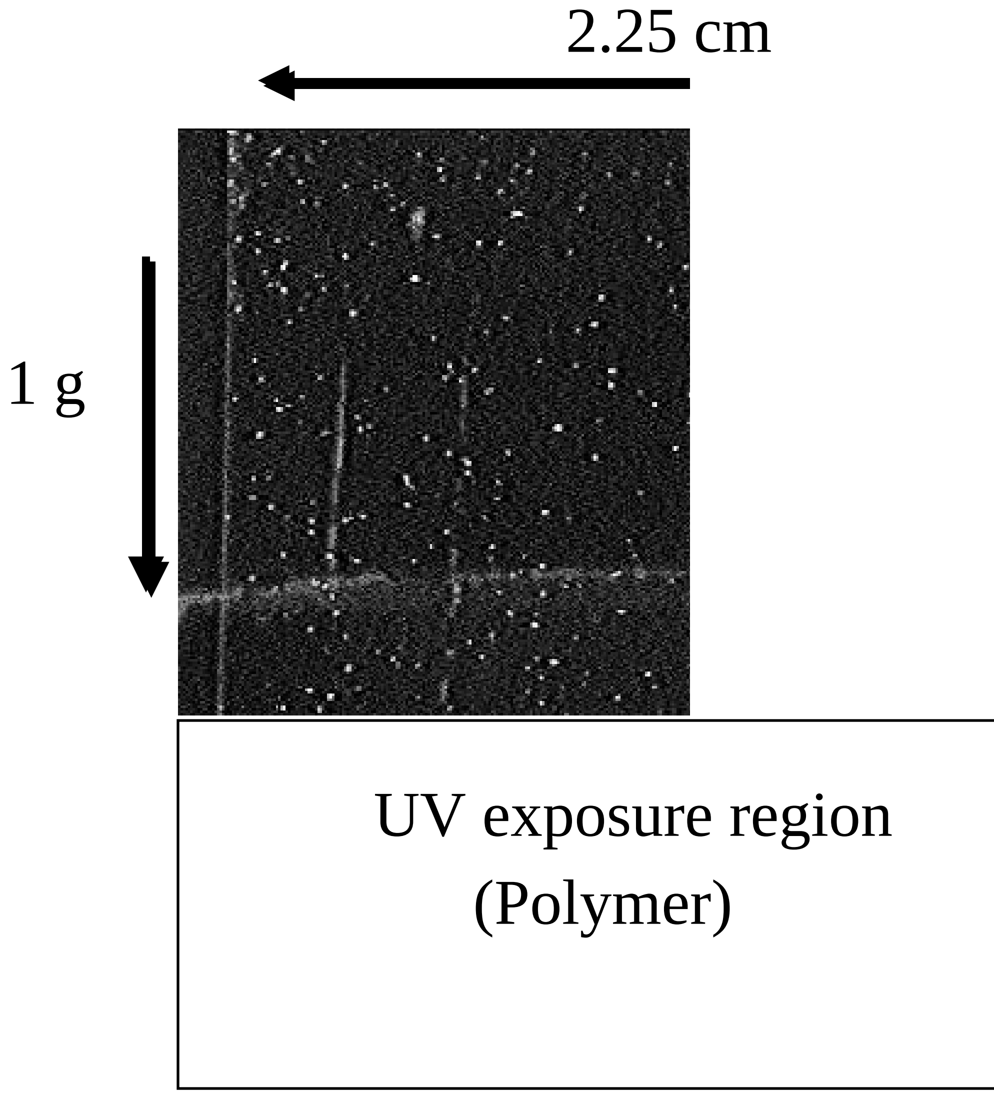

UV Light
Mask
Glass Cuvette
Polymer Concentration
0%
100%
3
Cuvette Height
0
Cuvette Length
6

Variable gradient



Why Microgravity?

buoyancy-driven convection destroys polymer/monomer transition



2.25 cm

1 g

UV exposure region
(Polymer)

Simulations

- add Korteweg stress terms in Navier-Stokes equations
- validate by comparison to steady-state calculations with standard interface model
- spinning drop tensiometry to obtain k
- theoretical estimates of k
- predict expected fluid flows and optimize experimental conditions

Model of Korteweg Stresses in Miscible Fluids

$$\frac{\partial T}{\partial t} + \mathrm{v} \quad T = \kappa \Delta T$$

$$\frac{\partial C}{\partial t} + \mathrm{v} \quad \alpha = D \Delta C$$

$$\frac{\partial \mathrm{v}}{\partial t} + (\mathrm{v} \quad)\mathrm{v} = -\frac{1}{\rho} \quad p + \nu \Delta \mathrm{v} + \frac{1}{\rho} \left\{ \begin{array}{l} \dfrac{\partial \mathrm{K}_{11}}{\partial x_1} + \dfrac{\partial \mathrm{K}_{12}}{\partial x_2} \\ \dfrac{\partial \mathrm{K}_{21}}{\partial x_1} + \dfrac{\partial \mathrm{K}_{22}}{\partial x_2} \end{array} \right.$$

div v = 0

$$K_{11} = k \left(\frac{\partial C}{\partial x_2} \right)^2$$

$$K_{12} = K_{21} = -k \frac{\partial \alpha}{\partial x_1} \frac{\partial C}{\partial x_2}$$

$$K_{22} = k \left(\frac{\partial C}{\partial x_1} \right)^2$$

where k is system sp

Navier-Stokes equations + Korteweg terms

Essential Problem: Estimation of Square Gradient Parameter “k”

- using spinning drop tensiometry
- use thermodynamics (work of B. Nauman)

Spinning Drop Technique

- Bernard Vonnegut, brother of novelist Kurt Vonnegut, proposed technique in 1942

Vonnegut, B. "Rotating Bubble Method for the Determination of Surface and Interfacial Tensions,"*Rev. Sci. Instrum.* **1942**, *13*, 6-9.

$$\boxed{\sigma = \frac{\Delta\rho\omega^2 r^3}{4}}$$

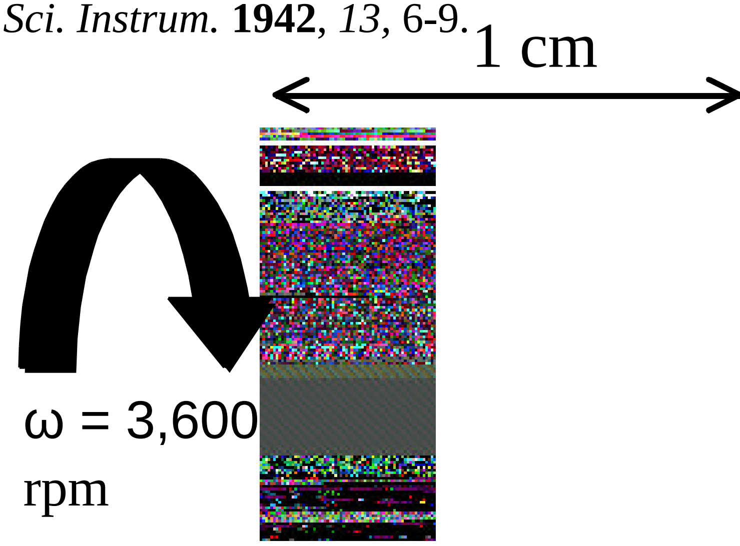
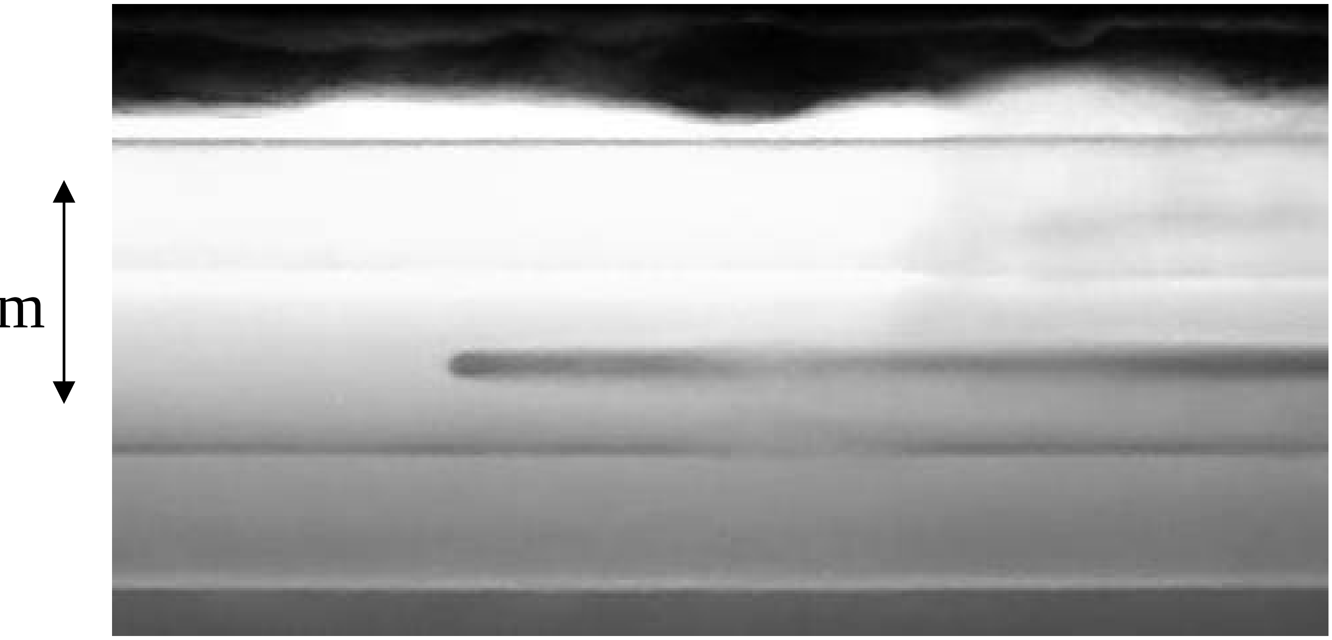
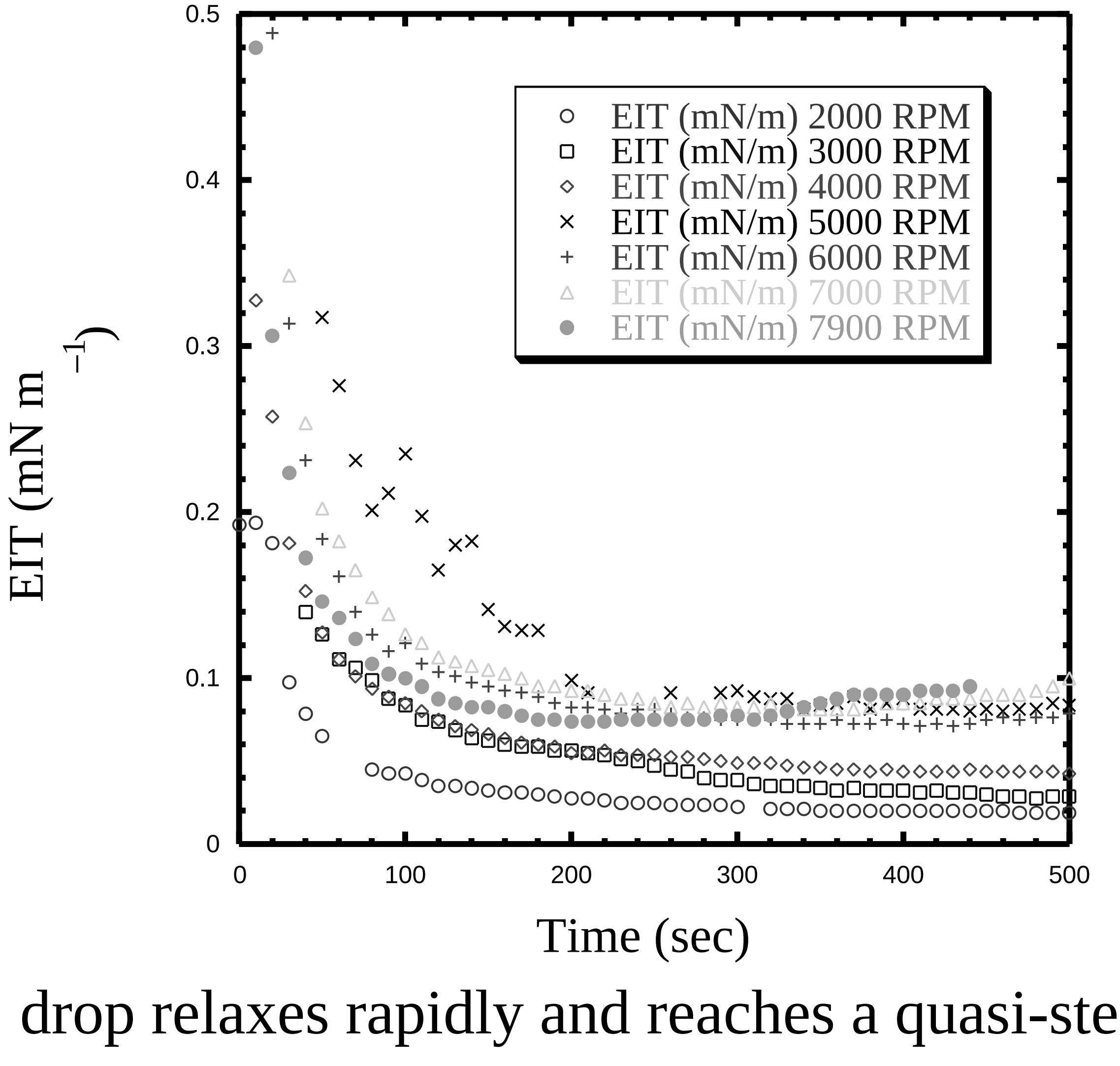


Image of drop



Evidence for Existence of EIT



drop relaxes rapidly and reaches a quasi-steady value

Estimation of k from SDT

- estimates from SDT: $k = 10^{-8}$ N
  - $k = EIT * \delta$
  - $k = 10^{-4}\ \mathrm{Nm}^{-1} * 10^{-4}$ m
- Temperature dependence
  - $\partial k/\partial T = -10^{-9}$ N/k
  - results are suspect because increased T increases diffusion of drop

Balsara & Nauman: Polymer-Solvent Systems

$$k = \frac{R_{gyr}^{2} RT}{6V_{molar}} \left[X + \frac{3}{1-C} \right]$$

X = the Flory-Huggins interaction parameter for a polymer and a good solvent, 0.45.

R_{gyr} = radius of gyration of polymer = 9×10^{-16} m^2

V_{molar} = molar volume of solvent

k = 5×10^{-8} N at 373 K

Balsara, N.P. and Nauman, E.B., "The Entropy of Inhomogeneous Polymer-Solvent Systems", *J. Poly. Sci.: Part B, Poly. Phys., 26*, 1077-1086 (1988)

Simulations

- Effect of variable transition zone, δ
- Effect of temperature gradient along transition zone
- Effect of conversion gradient along transition zone

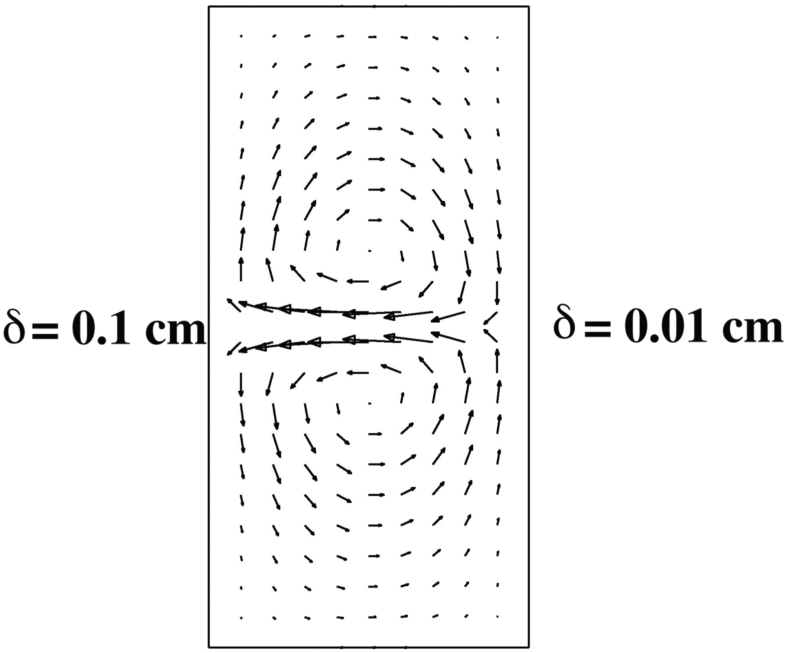
We validated the model by comparing to “true interface model”

- Interfacial tension calculated using Cahn-Hilliard formula:

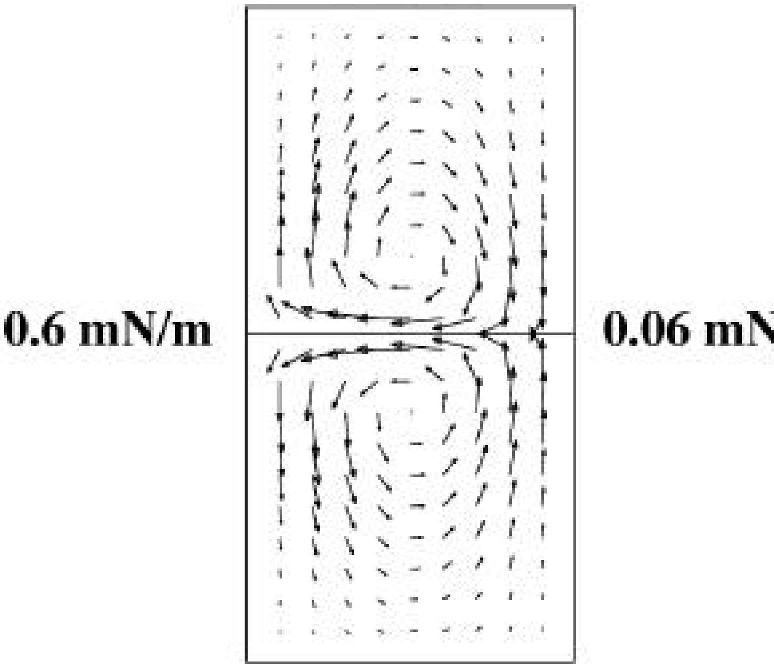
$$\sigma = k\frac{(\Delta C)^2}{\delta}$$

- same flow pattern
- Korteweg stress model exceeds the flow velocity by 20% for a true interface

Variation in δ



Korteweg

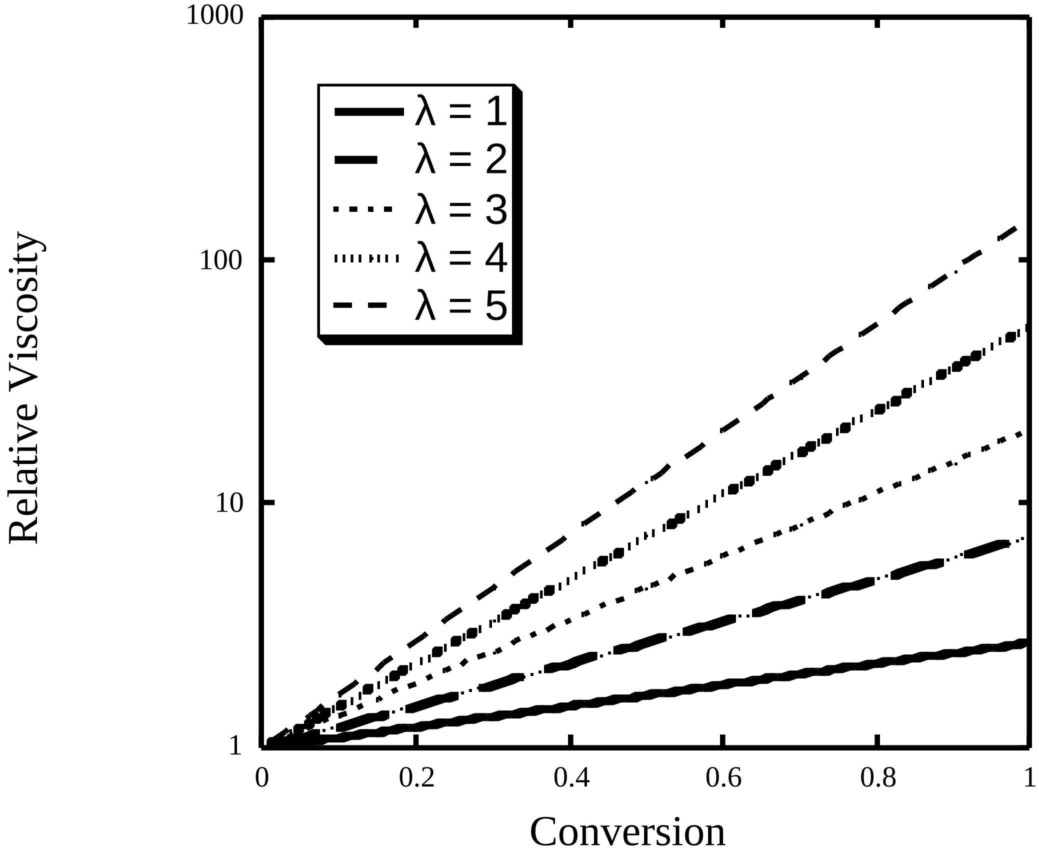


Interface

Simulation of Time-Dependent Flow

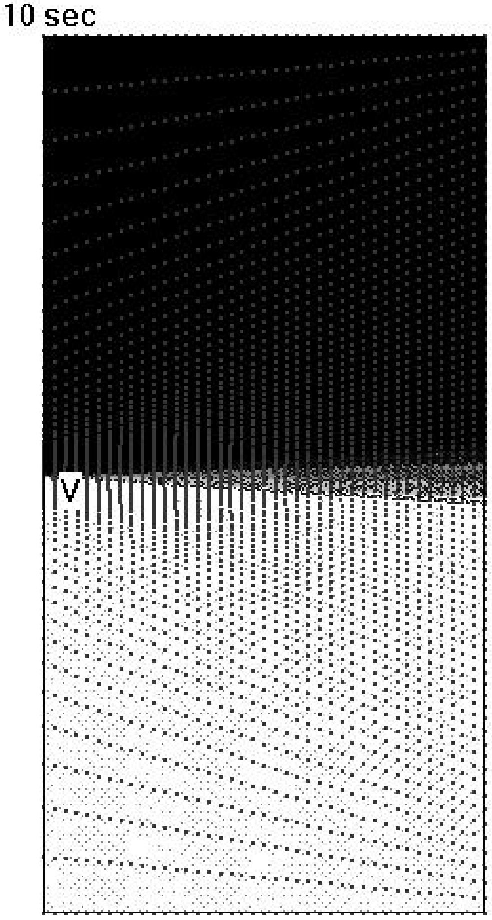
- we used pressure-velocity formulation
- adaptive grid simulations
- temperature- and concentration-dependent viscosity
- temperature-dependent mass diffusivity
- range of values for k

Concentration-Dependent Viscosity: $\mu = \mu_0 e^{\lambda c}$



λ = 5 gives
polymer tha
is 120 X mo
viscous thar
the monome

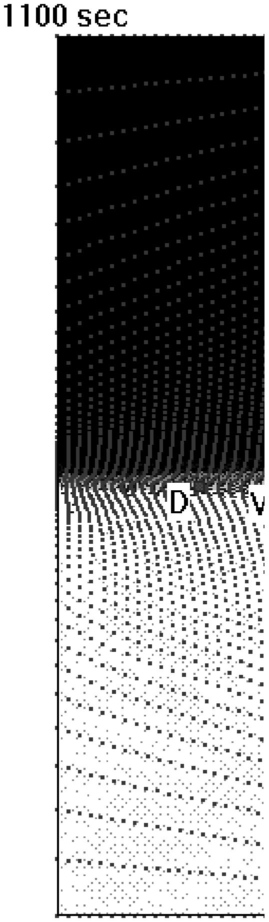
Variable transition zone, δ, 0.2 to 5 mm



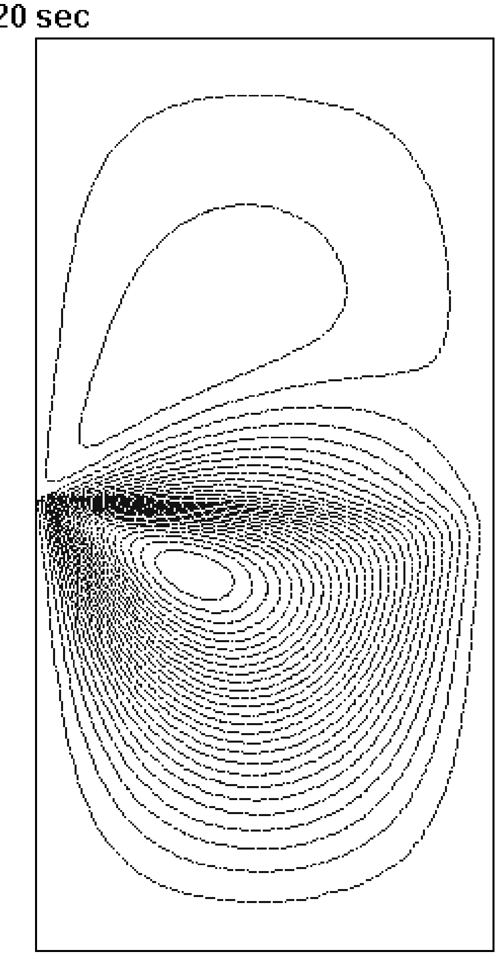
polymer

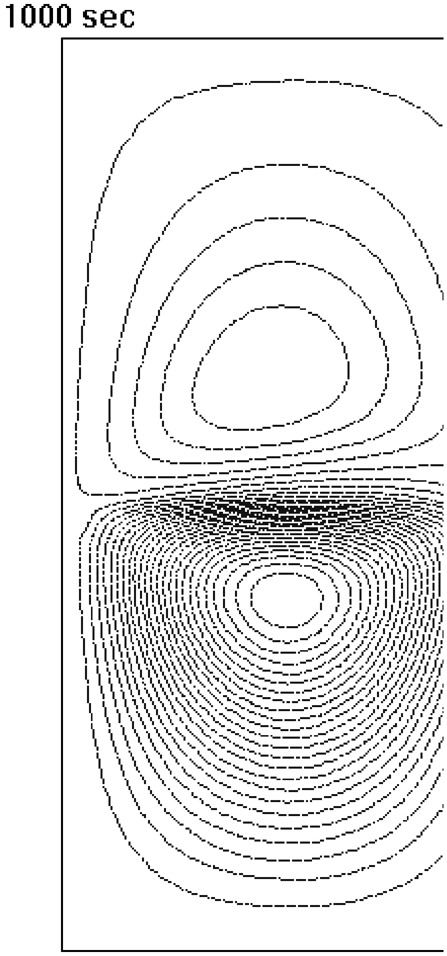
k = 2 x 10^{-9} N

monomer



streamlines

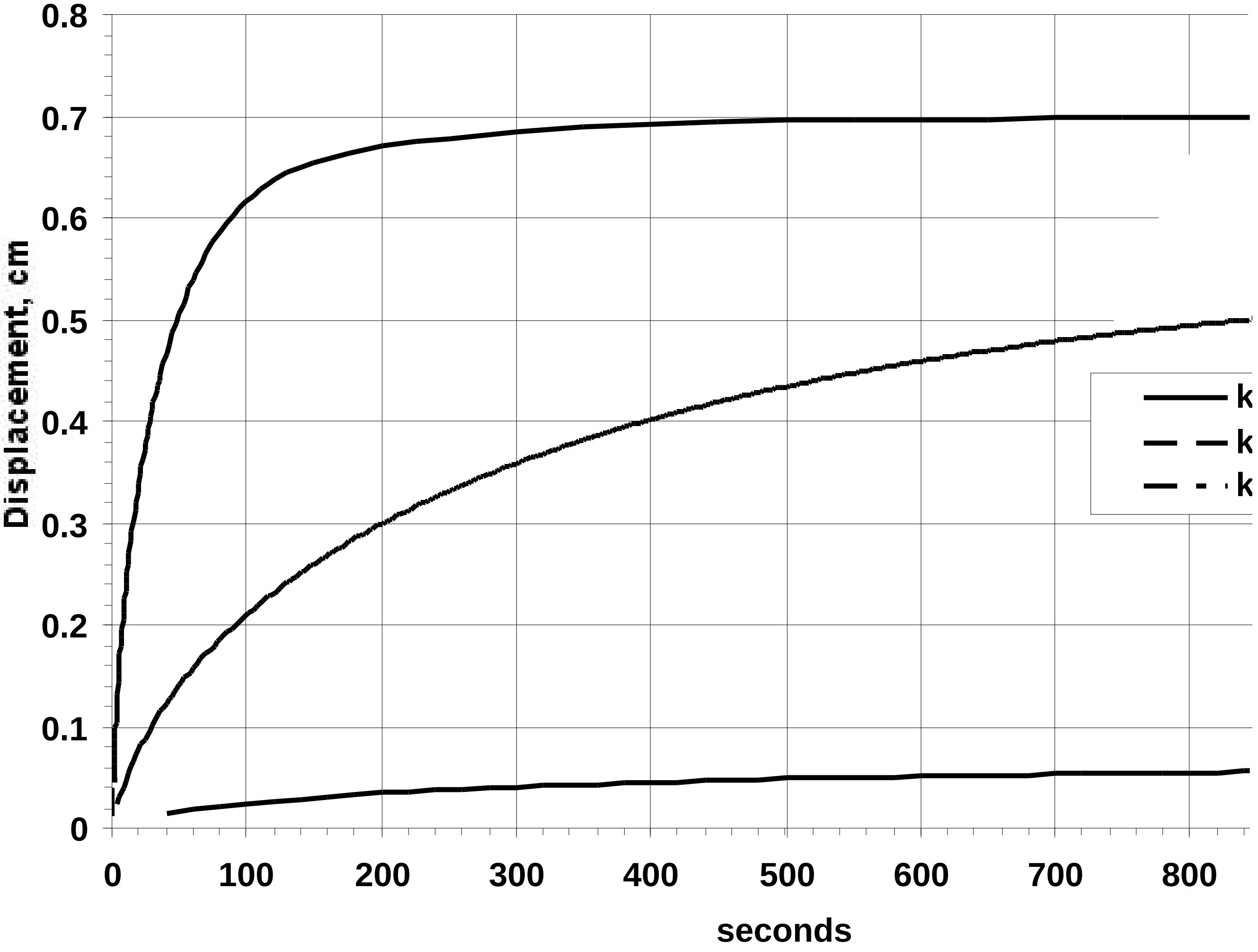




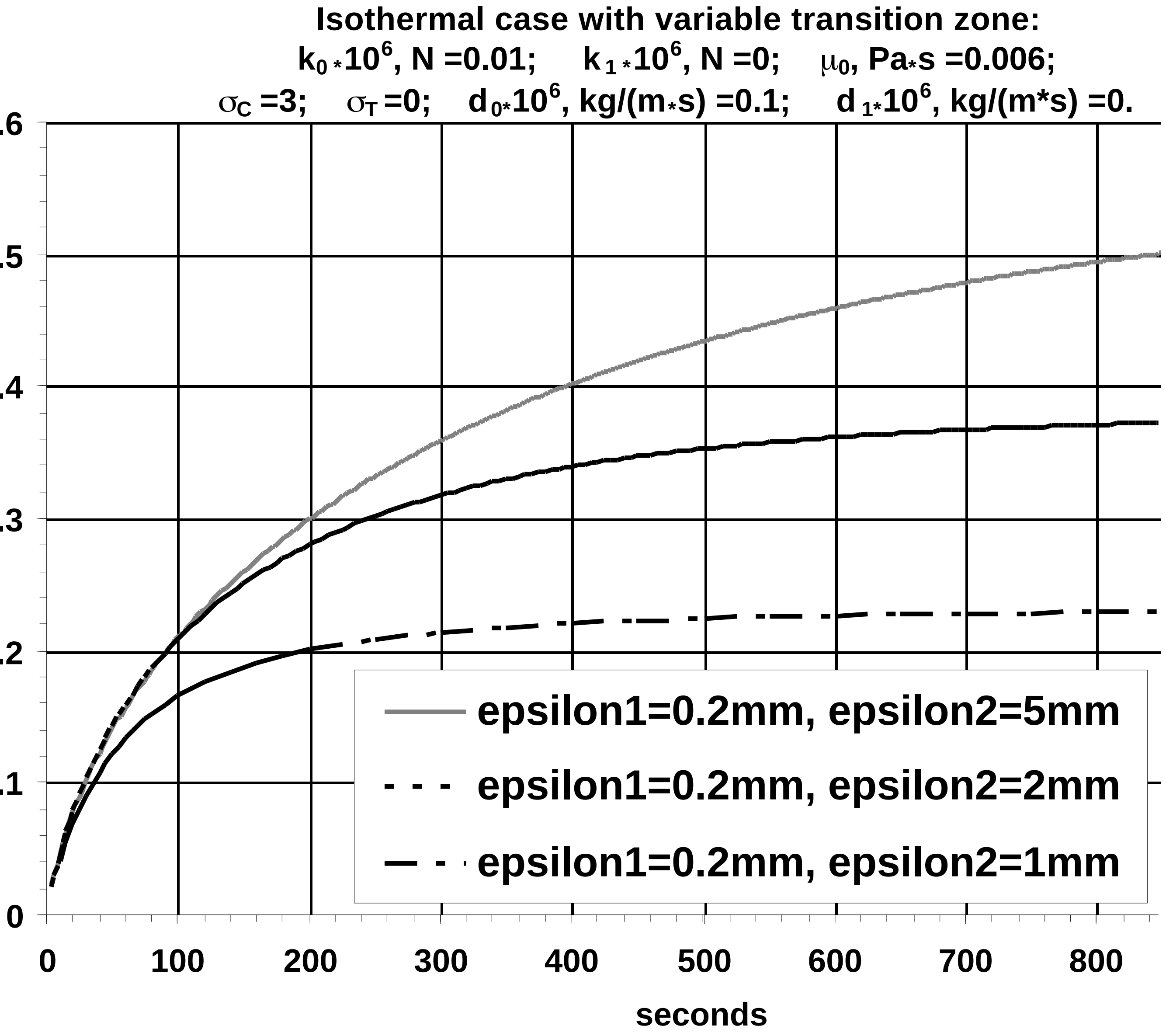
Maximum Displacement Dependenc on k

δ_1=0.2mm; δ_2=5mm; k_1*10^6, N =0; μ_0, Pa*s =0.006;

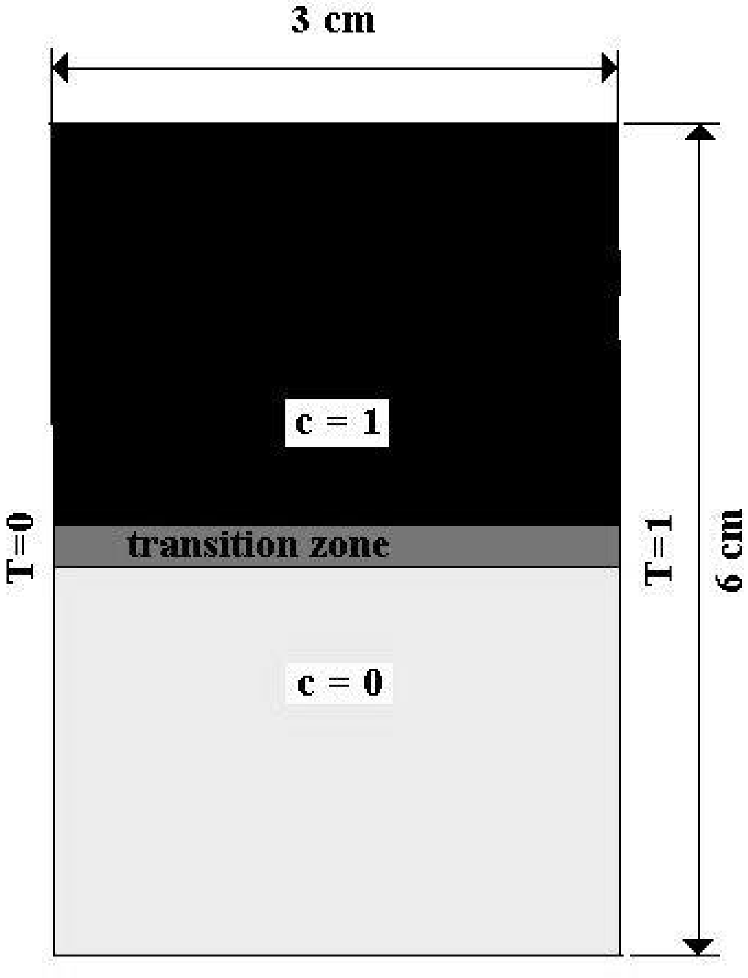
σ_C =3; σ_T =0; d_0*10^6, kg/(m*s) =0.1; d_1*10^6, kg/(m*s) =0.



Dependence on variation in δ



Effect of Temperature Gradient

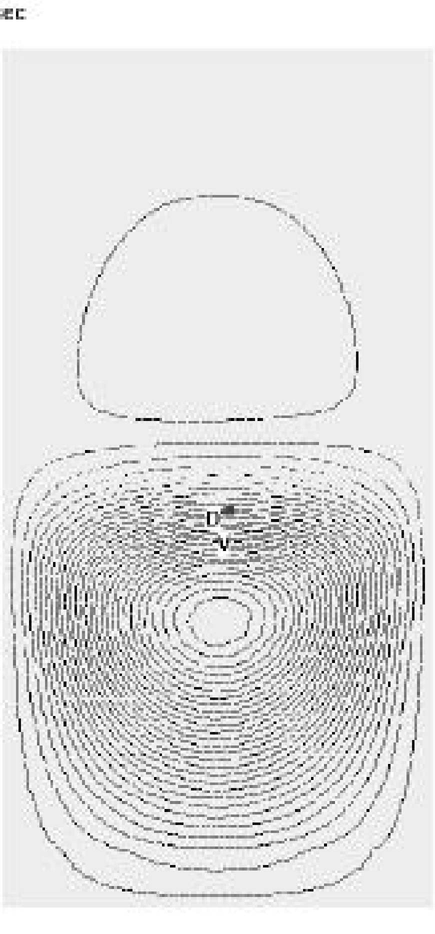


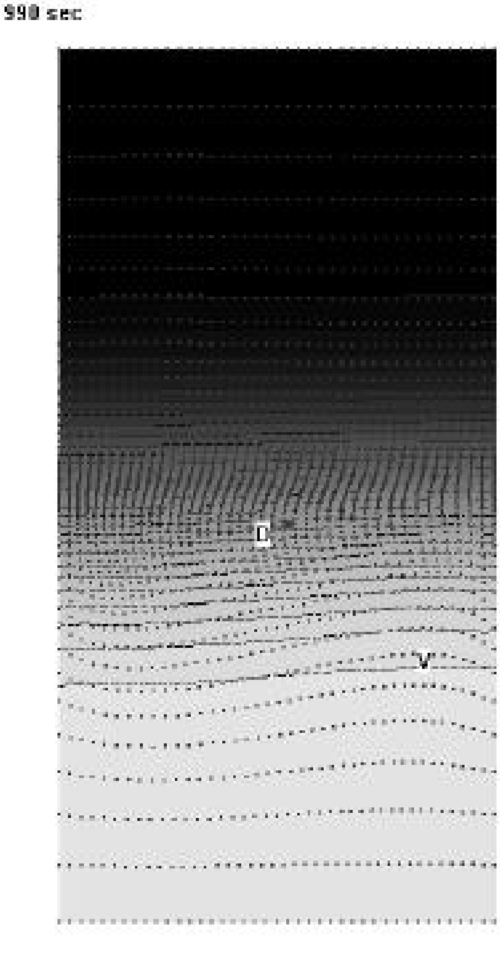
Temperature is scaled so T = 1 corresponds to ΔT = 50 K.

Simulations with different k(
-does it increase or decrease
with T?

Simulations with temperature
dependent diffusion
coefficient

viscosity 10X monomer (0.01 Pa s

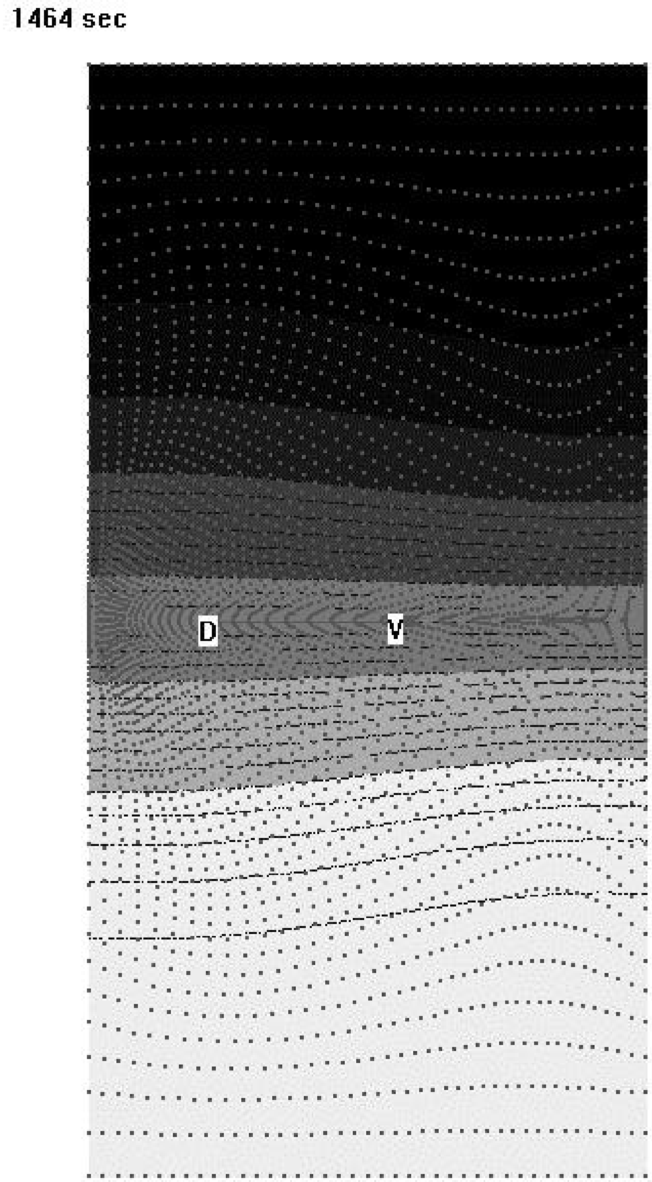




$k_0 = 1.3 \text{ x } 10^{-7}$

$k_1 = 0.7 \text{ x } 10^{-7}$ N

Two vortices are observed



e heating,
0.9 mm

T_0

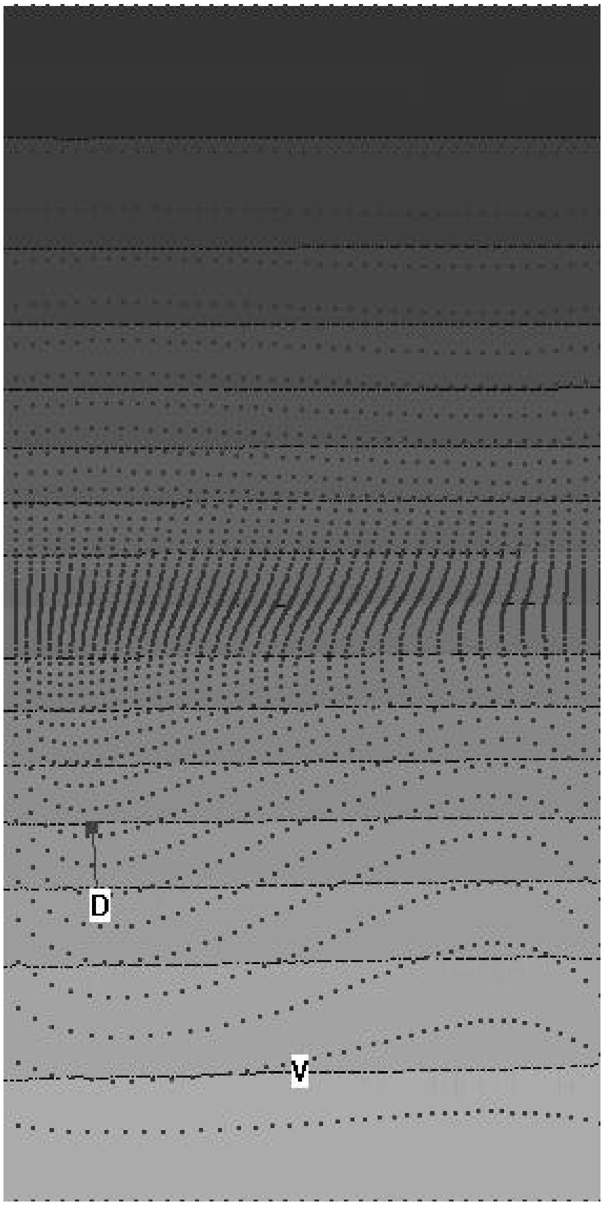
polymer
= 10 cm^2 s$^-$

T_0 + 50K

monomer
= 10 cm^2 s$^-$

asymmetric vortices are observed with variable viscosity model

e heating,
0.9 mm,
) =0 .01 Pa s * e$^{5\ c}$



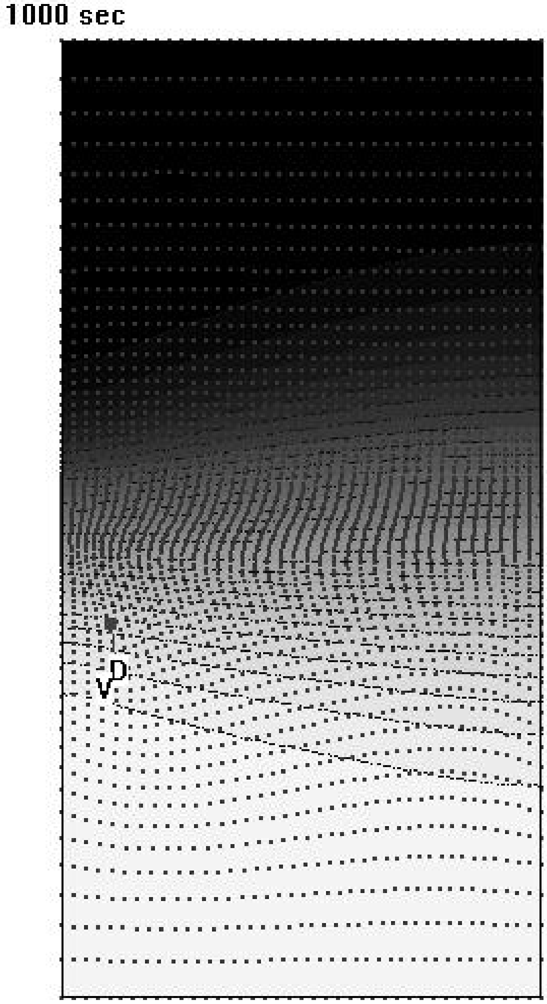
polymer
= 12 cm^2 s^{-}

monomer
= 0.1 cm^2 s

effect of temperature-dependent D

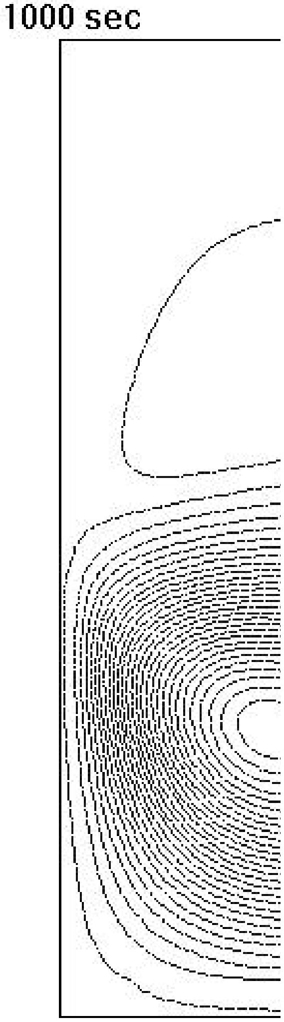
- k independent of T
- D increases 4 times across cell
- higher T means larger δ
- effect is larger than k depending on T even with viscosity 100 times larger

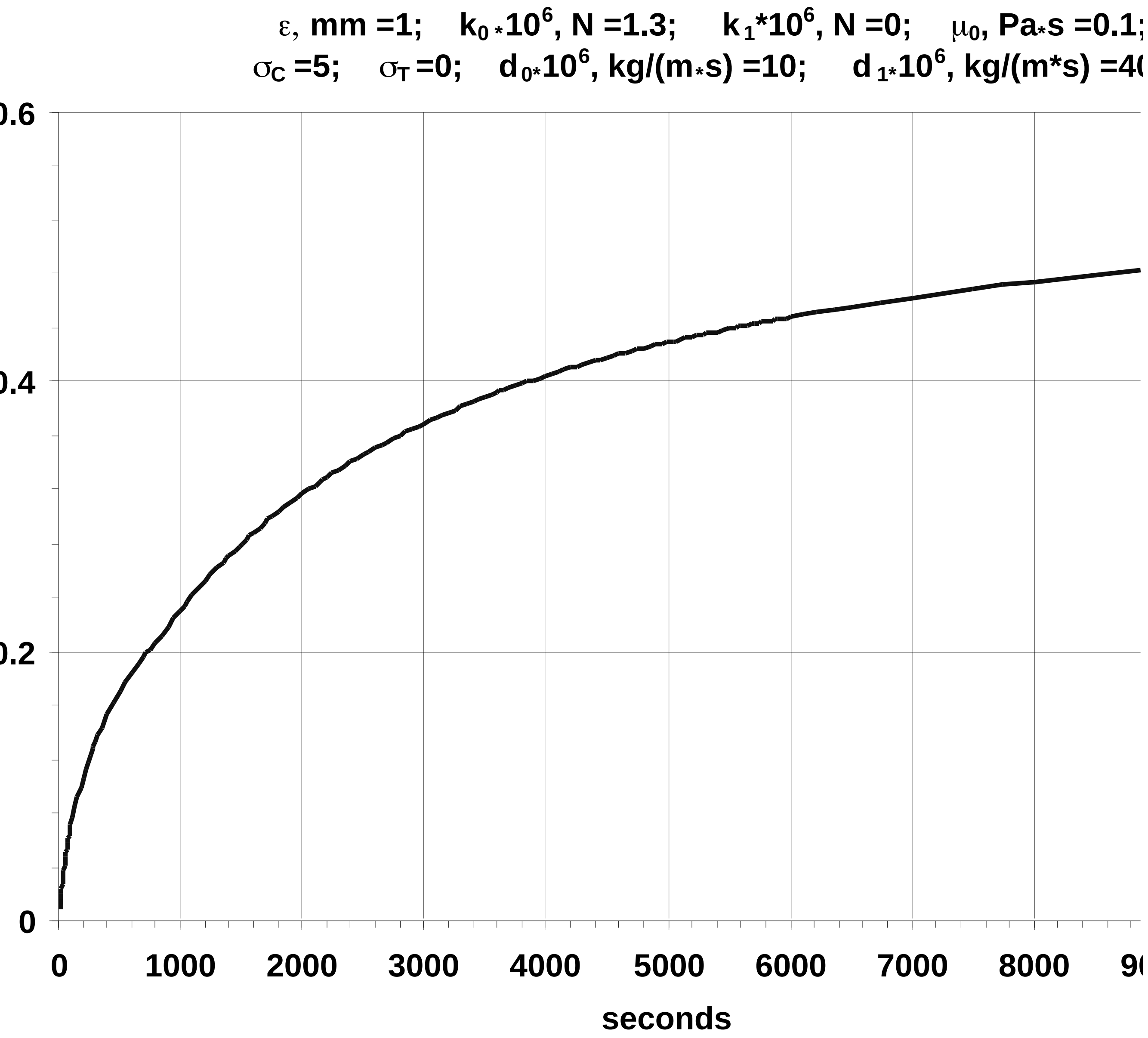
significant flow



T_1

T_0



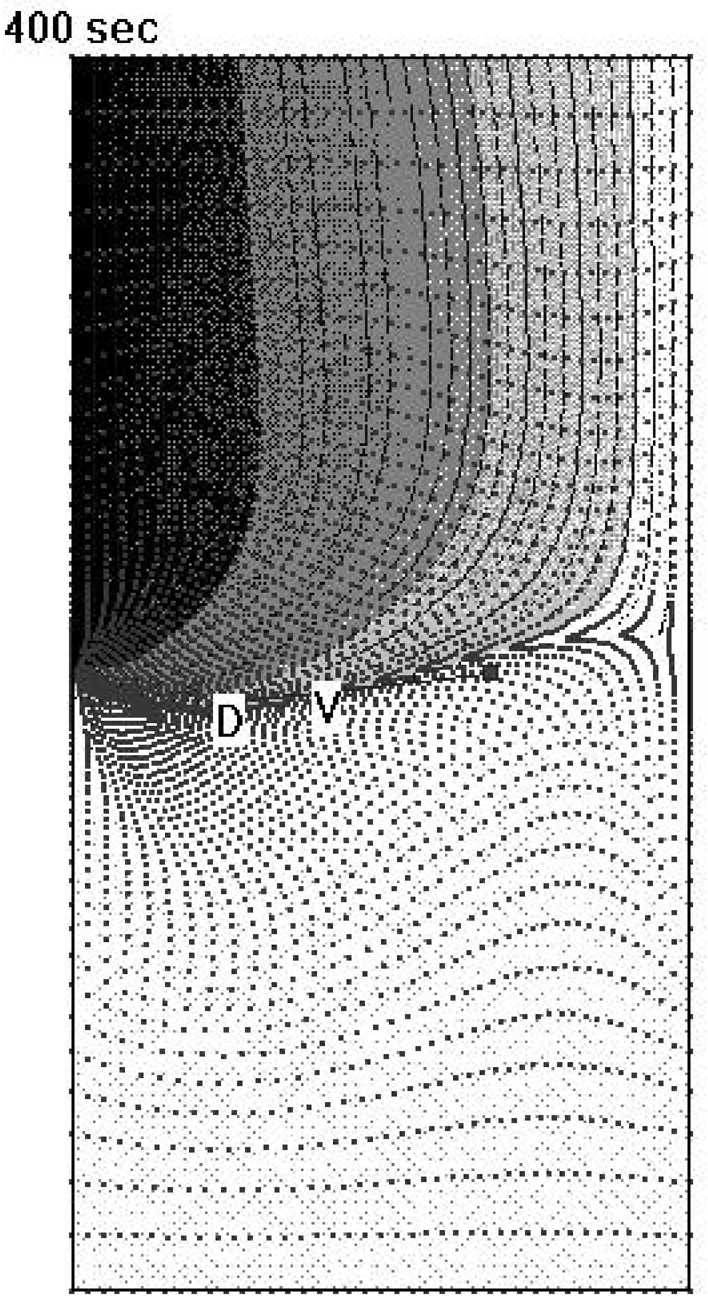


ε, mm =1; k_0*10^6, N =1.3; k_1*10^6, N =0; μ_0, Pa*s =0.1

σ_C =5; σ_T =0; d_0*10^6, kg/(m*s) =10; d_1*10^6, kg/(m*s) =4

Effect of Conversion Gradient

- T also varies because polymer conversion and temperature are coupled through heat release of polymerization
- T affects k
- T affects D



T = 150 ˚C

C =1

$k = 10^{-8}$ N

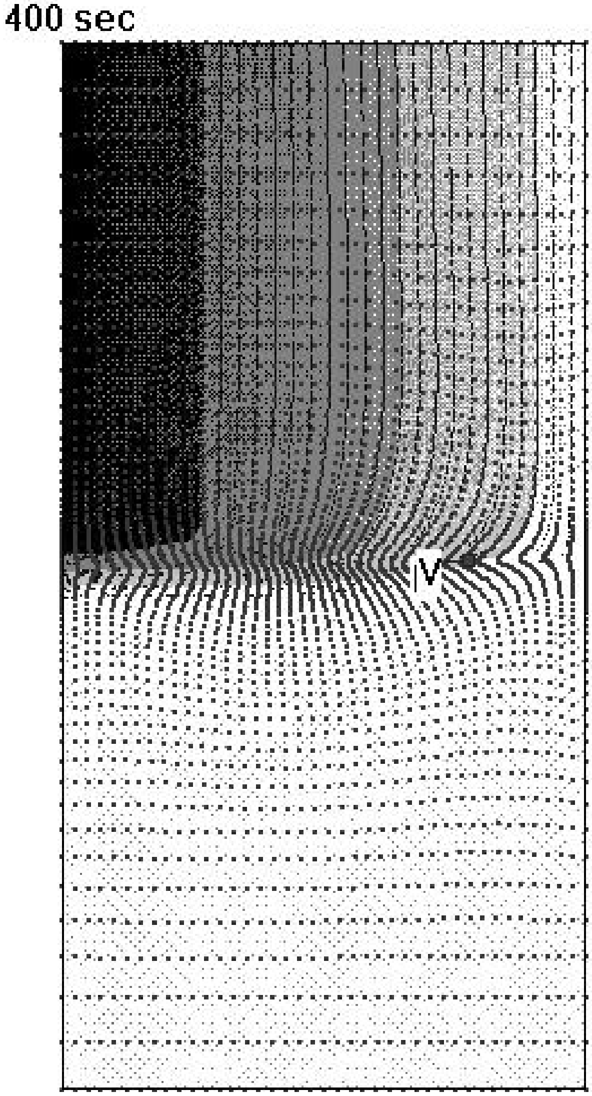
C =0

25 ˚C

polymer viscos
independent of

omer

with D(T)



C =1

k = 10^{-8} N

T = 150 ˚C

=1.2 x 10^{-5} cm^2 s^{-1}

C =0

T = 25 ˚C

D=1 x 10^{-6} cm^2 s^{-1}

monomer

Limitations of Model

- two-dimensional
- does not include chemical reaction
- neglects temperature difference between polymer and monomer
  - polymer will cool by conduction to monomer and heat loss from reactor

Conclusions

- Modeling predicts that the three TIPMPS experiments will produce observable fluid flows and measurable distortions in the concentration fields.
- TIPMPS will be a first of its kind investigation that should establish a new field of microgravity materials science.

Quo Vademus?

- refine estimations of “k” using spinning drop tensiometry
- completely characterize the dependence of all parameters on T, C and molecular weight
- prepare 3D model that includes chemistry
- include volume changes

Acknowledgments

- Support for this project was provided by NASA’s Microgravity Materials Science Program (NAG8-973).
- Yuri Chekanov for work on photopolymerization
- Nick Bessonov for numerical simulations