Relaxation Effects in the Modeling of Gradient Stresses

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The topics being discussed here are the physics and modeling of stresses due to gradients of composition

ϕ volume fraction of solute

Korteweg stresses $\qquad T_{ij}^{(2)} = \hat{\delta}\,\dfrac{\partial \phi}{\partial x_i}\,\dfrac{\partial \phi}{\partial x_j} + \hat{\gamma}\,\dfrac{\partial^2 \phi}{\partial x_i \partial x_j}$ (1)

Properties: (1) we may generate this by

$$T_{ij}^{(2)} = \frac{\partial^2 \Im[\phi]}{\partial x_j \partial x_i}$$ (2)

The stress depends on the *instantaneous* values of $\nabla \phi$

(ii) It is invariant to a change of frame, say to a change in the sign $\partial x_i \rightarrow -\partial x_i$

(iii) If we allow $T_{ij}^{(2)}$ to be an invariant function of $\partial \phi / \partial x_i$, and $\hat{\delta}$ and $\hat{\gamma}$ to functions of invariants we can get (1) using the Cayley-Hamilton theorem.

Equations

Composite density

$$\rho(\phi) = \rho_\gamma \phi + \rho_v (1 - \phi)$$

Mixtures of incompressible fluids are compressible

$$\frac{d\rho}{dt} = \frac{d\rho}{d\phi}\frac{d\phi}{dt} = (\rho_\gamma - \rho_v)\frac{d\phi}{dt}$$

Continuity equation
*div **u** ≠ 0 ρ_γ- ρ_v is most important*

$$(\rho_\gamma - \rho_v)\frac{d\phi}{dt} + \rho \, \text{div } \mathbf{u} = 0$$

Diffusion equation

$$\frac{d\phi}{dt} + \phi \, \text{div } \mathbf{u} = \text{-div}\mathbf{q}_\gamma$$

Ficks law

$$\mathbf{q}_\gamma = -D_\gamma(\phi)\nabla\phi$$

Momentum

$$\rho\frac{d\mathbf{u}}{dt} = -\nabla\pi + \rho\mathbf{q} + \text{div}\left(\mathbf{T}^{(1)} + \mathbf{T}^{(2)}\right)$$

$$\mathbf{T}^{(1)} = 2\mu\mathbf{D}[\mathbf{u}] - \frac{2}{3}\mathbf{1}\mu \, \text{div } \mathbf{u}$$

$$\mathbf{T}^{(2)} = \text{Korteweg stress}$$

Transient interfacial
tension between miscible liquids

Freundlich (1926)

…We have only to remember here we are in the end always dealing with solutions. For the one liquid will always be soluble in the other to some degree, however, small. Hence the *dynamic* tension of liquids, when first brought into contact, is to be distinguished from the *static* tension, when the two liquids are mutually saturated. Not only do liquids which are not miscible in all proportions have a mutual surface tension; even two completely miscible liquids, before they have united to form one phase, exhibit a dynamic interfacial tension. For we get by careful overlaying of any two liquids a definite meniscus, a jet of one liquid may be generated in another, and so on. The tension decreases rapidly during the process of solution, and becomes zero as soon as the two liquids have mixed completely.
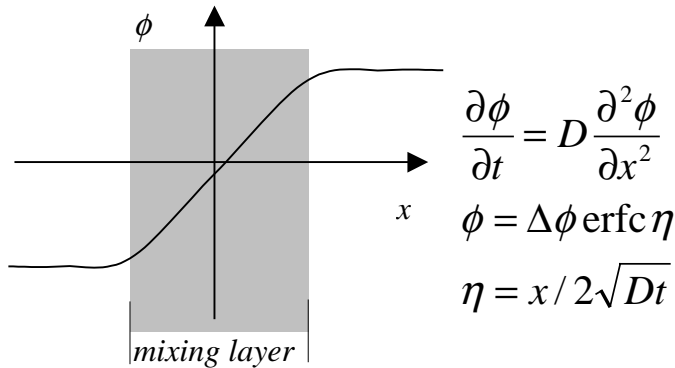
A few attempts were made to measure the tension at early times *t*.
Quinke (1902) got 0.8-3.0 dyn/cm for ethyl alcohol/salt water. Smith *et al* (1981) got 1 dyn/cm for 1 cs/2000 cs silicone oil.

A theory of tension at a miscible displacement front

by H. Ted Davis, 1988

$$\gamma = \int_{-\infty}^{\infty} \Delta P \, \mathrm{d}x \qquad \textit{Tension}$$

Mixing layer $\phi \to 0$ as $t \to \infty$.

mixing layer

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2}$$

$$\phi = \Delta\phi \, \mathrm{erfc}\, \eta$$

$$\eta = x / 2\sqrt{Dt}$$

He uses the Irving-Kirkwood pressure tensor to evaluate ΔP

ΔP jump in the normal stress across the mixing layer

$$\gamma = \int_{-\infty}^{\infty} \left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2 \mathrm{d}x$$

$C = 10^{-5}$ dyn for hydrocarbon mixtures

$$\gamma = \frac{C\Delta\phi^2}{2\sqrt{2\pi Dt}}$$

Table 1. Tension γ of a planar front of a miscible fluid as a function of time t of diffusive spreading of the front*.

Time	Mixing Zone Width $\sqrt{Dt}$ (cm)			Tension γ(dyn/cm)		
	$D = 10^{-5}$ cm^2/s	$D = 10^{-7}$ cm^2/s	$D = 10^{-9}$ cm^2/s	$D = 10^{-5}$ cm^2/s	$D = 10^{-7}$ cm^2/s	$D = 10^{-9}$ cm^2/s
1	3.1×10^{-3}	3.1×10^{-4}	3.1×10^{-5}	6.3×10^{-4}	5.3×10^{-3}	5.3×10^{-2}
10	10^{-2}	10^{-3}	10^{-4}	2.0×10^{-4}	2.0×10^{-3}	2.0×10^{-2}
10^2	3.1×10^{-2}	3.1×10^{-2}	3.1×10^{-3}	6.3×10^{-5}	5.3×10^{-4}	5.3×10^{-3}
10^3	10^{-1}	10^{-2}	10^{-4}	2.0×10^{-5}	2.0×10^{-4}	2.0×10^{-3}
4×10^3	2×10^{-3}	2×10^{-3}	2×10^{-3}	1.0×10^{-5}	1.0×10^{-4}	1.0×10^{-3}

"From the entries in this table it follows that the tension of a diffusive mixing zone between miscible liquids while small, is nevertheless not zero."

*The value $c(\phi_2 - \phi_b)^2 / 2\sqrt{2x} = 2\times10^{-6}$ dyn was used.

Joseph *et al* 1990-1996

- Joseph *et al* used the full set of basic equations for mixing liquids to study transient tension.

  - The Korteweg stresses do not enter into the jump of normal stress ΔP at a plane layer

  - At a spherical layer centered on r_0

$$\Delta P = \frac{2}{r_0}\sqrt{\frac{D}{t}}\left(164\frac{-\hat{\delta}}{D} - 429\right)$$

to get positive tension $\hat{\mathbf{g}} < 0$

Interfacial tension in miscible two-fluid systems with linear viscoelastic rheology,

by J.E. Mungall. *Physical Review Letters*, **73**(2), 1994.

I present observations of interfacial tension between miscible pairs of silicate liquid and propose a theoretical model that quantitatively accounts for them. Viscoelastic rheology of the liquids permits the establishment of gradient stress completely analogous to thermal stress in Maxwell solids; this is expected whenever the time scale of diffusion is shorter than the Maxell relaxation time. The existence of gradient stress may profoundly affect interface processes during the mixing of miscible fluids.

…Observed interfacial tension in molten silicates at 1300°C and 1 bar pressure ... they correspond to the natural lava types trachyte (*P16a*) and basalt (146). Each experiment consisted of a block of basaltic glass situated underneath a block of trachytic glass, in contact at a polished planar horizontal interface, in an open Pt crucible. The finished assembly was hung with Pt wire within the hotspot of the 1 atm tube furnace and brought to temperate within 2 min. One experiment was quenched immediately upon reaching the run temperature of 1300°C whereas the others had durations of 17 and 84 min. after reaching 1300°C…

Backscattered scanning electron micrographs of vertical sections through the run products are shown in Figure 1 [in the next slide].

…At the time of first melting of the glasses the interface was perfectly planer. The interface as it appeared after quench is clearly visible and in all four experiments forms a meniscus (see figure caption). ***In the reversed experiment the sense of curvature of the meniscus is also reversed*** [our emphasis]. Since basaltic and trachytic liquids are completely miscible, the classic concept of a surface tension cannot be applied to this case.

Back-scattered Electron Micrographs of Results of Experiments
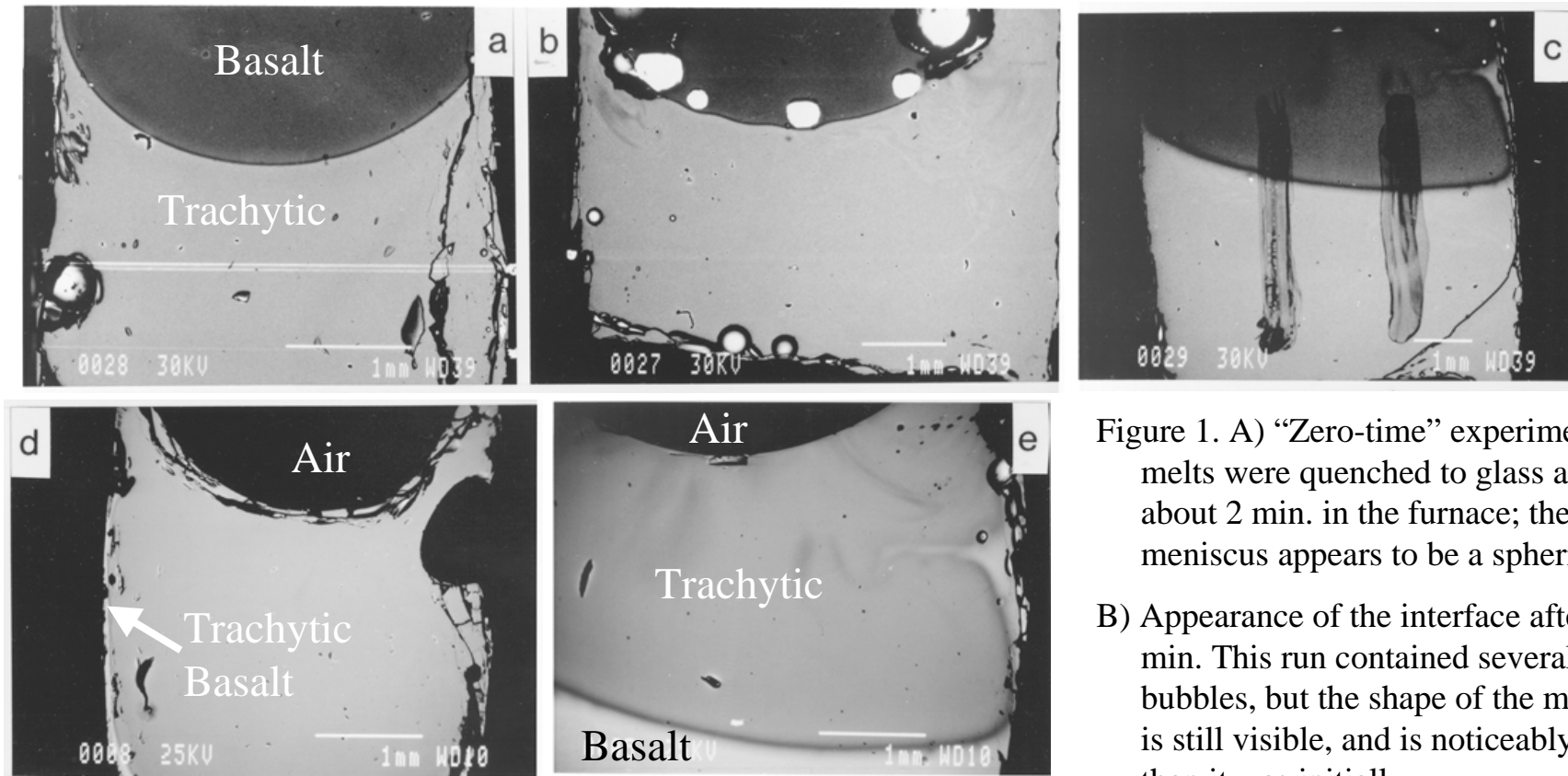

Figure 1. A) "Zero-time" experiment. The melts were quenched to glass after about 2 min. in the furnace; the meniscus appears to be a spherical cap.

B) Appearance of the interface after 17 min. This run contained several bubbles, but the shape of the meniscus is still visible, and is noticeably flatter than it was initially.

C) The interface after 84 min. is nearly flat, reflecting a radical decrease in interfacial tension.

D) Portion of the zero time experiment immediately above that featured in part A). Note the thin mantle of basalt that completely wets the Pt wall along the right. The right side is also completely wetted, although it is less obvious in the photo.

E) Detail of the completely wetted wall after 84 min.; interfacial tension has diminished sufficiently to allow weak convective flows in the trachytic melt to disrupt the interface and pull basaltic material into it. The convective flow resulted from density contrasts between the basaltic and trachytic melts. This was discussed at greater length by Mungall 1993.

J.E. Mungall. *Physical Review Letters*, **73**(2), 1994

- The transient interfacial effects observed in Mungall's experiments are possibly too long lasting to be explained by the conventional Korteweg theory.

- I think he is right to introduce relaxation although I will introduce it somewhat differently.

Stability of Al_2O_3-containing Droplets in Glass Melts

by Sabin Rung and G.G. Frischat,

Al_2O_3-contaiing droplets ("model cords") were placed on an Al_2O_3-free matrix glass of the system Na_2O-CaO-SiO_2 and were allowed to sink in and react with the glass melt. From a comparison using Al_2O_3-free substances it could be shown that the Al_2O_3-containing droplets achieved characteristic rotationally-symmetric contours, which can be explained only by assuming an acting interfacial energy in the contact zone between the two glass melts. From the droplet contours an effective interfacial tension between 0.4 and 1.1 mN m^{-1} could be calculated. The interdiffusion profiles in the contact zone showed that although Al_2O_3 and SiO_2 equilibrated slowly by diffusion, both Na_2O and CaO withstand equilibration by uphill diffusion. *In conclusion, both the effective interfacial energy and the uphill diffusion prevent a rapid dissolution of Al_2O_3-containing cords* [our emphasis.]

Glass melts have high viscosity and low diffusion.
Are relaxation effects important?

Stability of droplets in glass melts
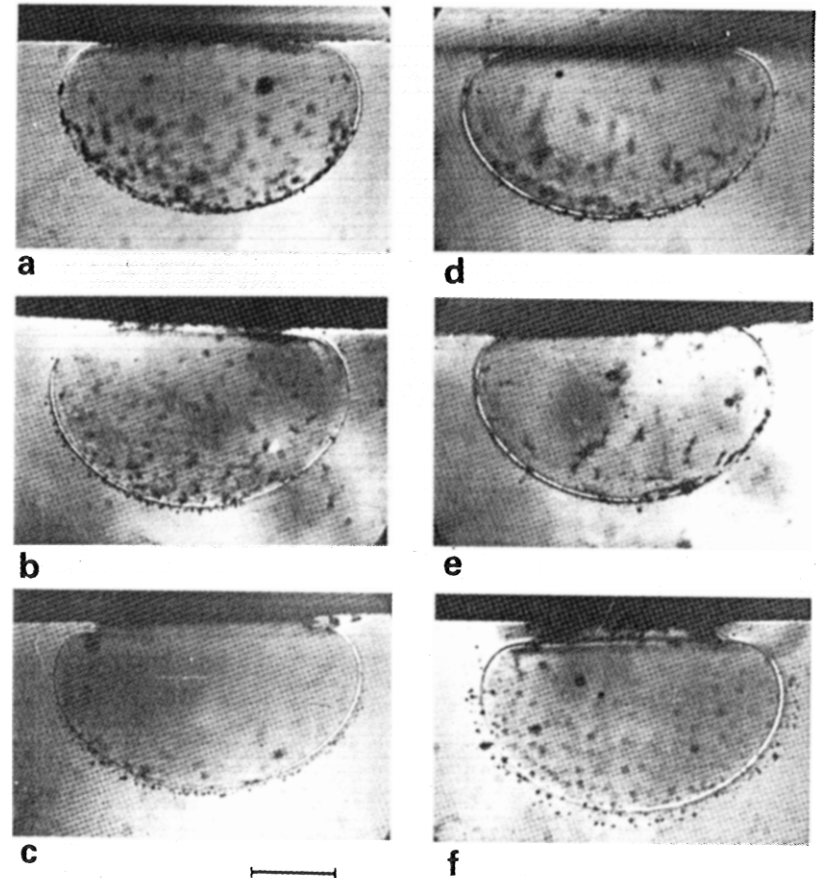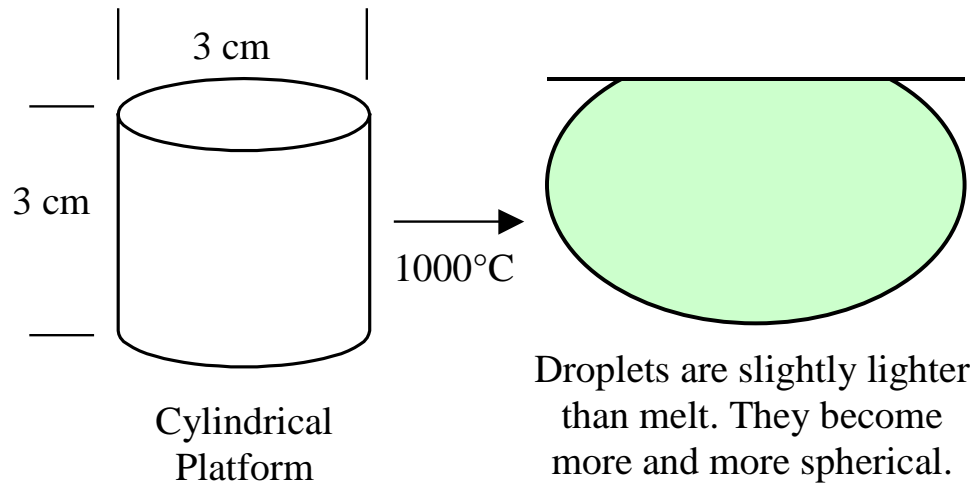
(S. Runge, G.H. Frischat 1988.)

3 cm

3 cm

1000°C

Cylindrical
Platform

Droplets are slightly lighter
than melt. They become
more and more spherical.

*Figure 3. [at right] Droplets after sink-in
experiments at u_{max} = 996°C, similar
conditions as in [their] figure 2;
(a) th = 0, (b) 7.5, (c) 15, (d) 30, (e) 45,
and (f) 60 min. respectively. Bar = 1 mm.*

Effective tension 0.4 – 1.1 dyn/cm for lighter-than-glass Al_2O_3 droplets in glass melts.
The drop shape on the bottom is more spherical after an hour but eventually they mix
completely.

Comparison of droplets with and without Al$_2$O$_3$
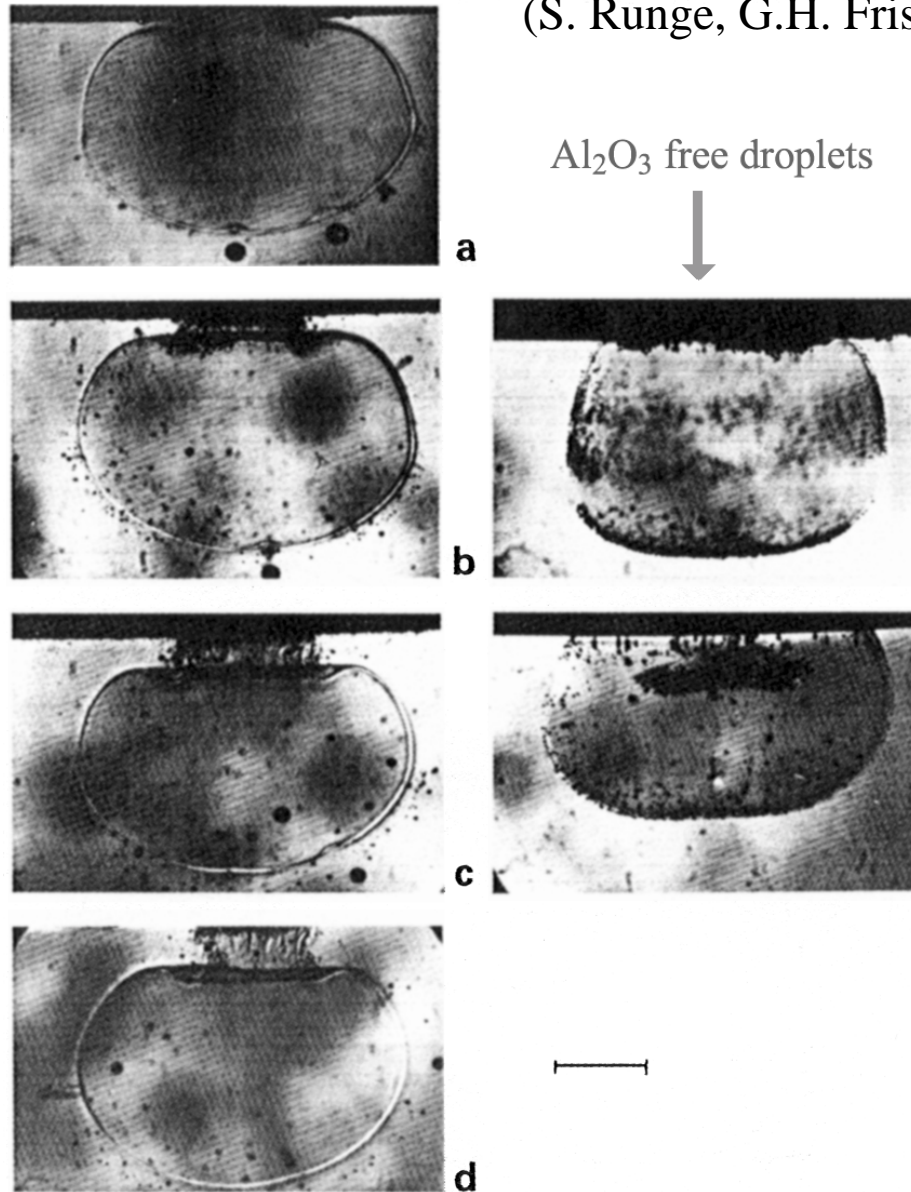
(S. Runge, G.H. Frischat 1988.)

Al$_2$O$_3$ free droplets

Figure 6. Droplets after nearly totally dipped cord preforms at v_{max} = 1045°C, cylinderic droplet preforms of 3 mm in height and 3 mm in diameter, matrix Al$_2$O$_3$-free glass, droplet Al$_2$O$_3$-containing glass (left column) and Al$_2$O$_3$-free glass (right column), respectively. Before dipping the matrix melt was held at v_{max}. (a) t$_h$ = 15, (b) 30, (c) 45, and (d) 60 min, respectively. Bar = 1 mm.

- I did some experiments on tension between polymer melts for Sumitomo. At the high temperatures of the measurement the melts appeared to be miscible.

t_1

Ω

t_2

Ω

Later

- At each t, I could measure a different tension. These melts have relaxation effects.

ϕ

Sharp interface :
$\phi \rightarrow 0$ at $t \rightarrow \infty$

x

- The effects of transient tension are enhanced by relaxation effects
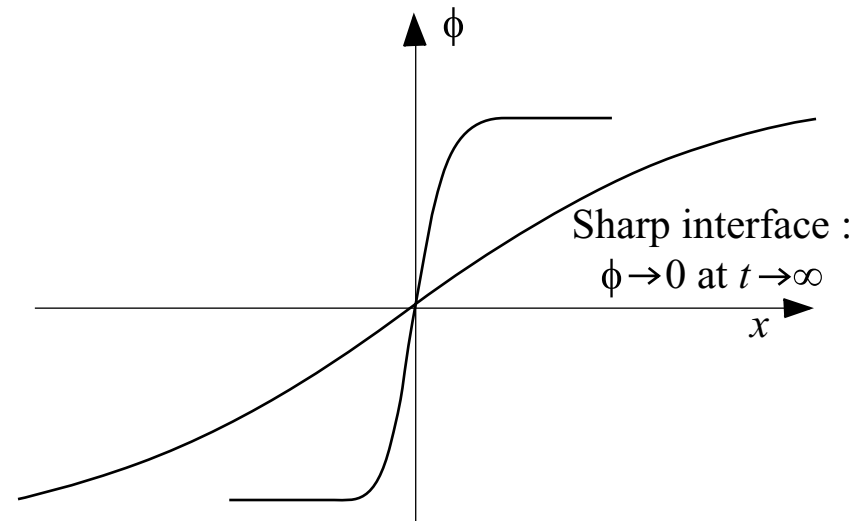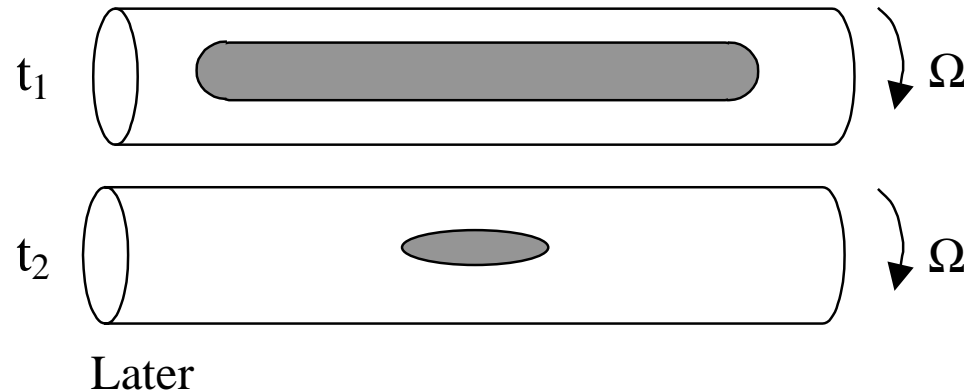
Stress Relaxation : A sharp interface produces a stress. It takes time for this stress to relax

Composition Relaxation : A sharp interface produces a stress. It takes time for the interface to relax

Stress Relaxation

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \pi + \rho \mathbf{q} + \text{div}\left(\mathbf{T}^{(1)} + \mathbf{T}^{(2)}\right)$$

$\mathbf{T}^{(1)}$ due to motion

$\mathbf{T}^{(2)}$ due to composition

- Maxwell relaxation

$$\lambda_1 \overset{\nabla}{\mathbf{T}^{(1)}} + \mathbf{T}^{(1)} = 2\mu \mathbf{D}[\mathbf{u}] - \frac{2}{3}\mathbf{1}\pi \, \text{div} \, \mathbf{u}$$

$$\lambda_2 \overset{\nabla}{\mathbf{T}^{(2)}} + \mathbf{T}^{(2)} = \hat{\delta} \nabla \phi \otimes \nabla \phi + \nabla \otimes \nabla \phi$$

- Various invariant derivatives may be used.
  We may also implement Oldroyd type models.

Composition Relaxation

- Simplest case

$$\frac{\partial \phi}{\partial t} = -\operatorname{div} \mathbf{q}_\phi \qquad \textit{Diffusion equation}$$

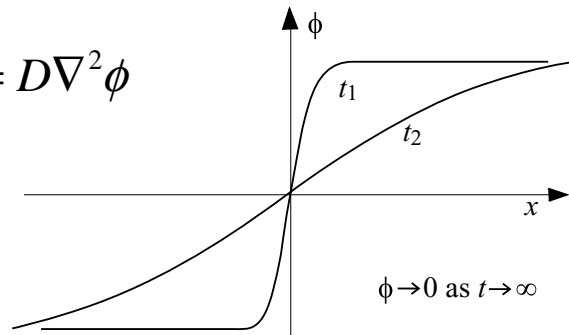$$q_\phi = -D\nabla\phi \qquad \textit{Ficks law}$$

$$\frac{\partial \phi}{\partial t} = D\nabla^2\phi \qquad \textit{Parabolic equation}$$

$$\lambda_3 \frac{\partial^2 \phi}{\partial t} + \frac{\partial \phi}{\partial t} = D\nabla^2\phi \qquad \begin{array}{l}\textit{Telegraph equation.}\\ \textit{Decaying wave}\end{array}$$

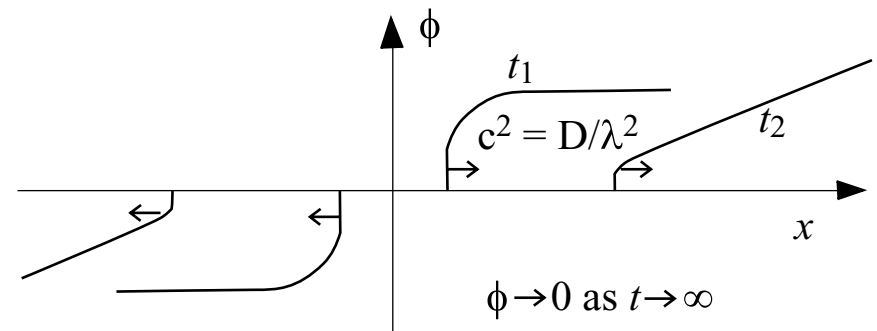$\phi \to 0$ as $t \to \infty$

- Suppose we have relaxation instead of Ficks law,

$$\lambda_3 \frac{\partial q_\phi}{\partial t} + q_\phi = -D\nabla\phi$$

$$\lambda_3 \frac{\partial^2 \phi}{\partial t^2} + \frac{\partial \phi}{\partial t} = D\nabla^2\phi$$

$$\frac{\partial \phi}{\partial t} = D\nabla^2\phi$$

$\phi \to 0$ as $t \to \infty$

$$\frac{\partial \phi}{\partial t} + \phi \operatorname{div} \mathbf{u} = -\operatorname{div} \mathbf{q}_\phi$$

$$\lambda_3 \overset{\triangledown}{\mathbf{q}}_\phi + \mathbf{q}_\phi = -D_\gamma(\phi)\nabla\phi$$

- $\overset{\triangledown}{\mathbf{q}}$ is an invariant derivative of a vector. These derivatives are discussed on pages 13-14 of my book *Fluid Dynamics of Viscoelastic Liquids* (Springer, 1990)