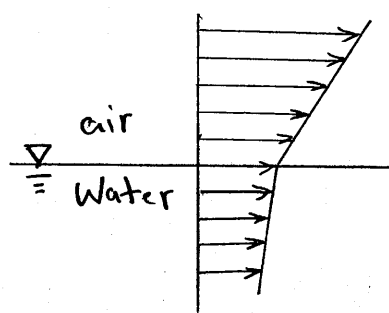


Generally, the boundary conditions on any gas-liquid interface are taken to be that both the velocity and the tangential stress are continuous at the interface, since both fluids possess some viscosity



Example:  
Wind blowing  
across Water  
Surface

$$\text{at } y=0, \quad u_{\text{air}} = u_{\text{water}}$$

$$\text{and } \tau_{\text{air}}^0 = \tau_{\text{water}}^0 \quad \leftarrow \text{at surface}$$

$$\Downarrow$$

$$\mu_{\text{air}} \left. \frac{\partial u}{\partial y} \right|_{y=0}^{\text{air}} = \mu_{\text{water}} \left. \frac{\partial u}{\partial y} \right|_{y=0}^{\text{water}}$$

$$\Rightarrow \left. \frac{\partial u}{\partial y} \right|_{y=0}^{\text{water}} = \frac{\mu_{\text{air}}}{\mu_{\text{water}}} \left. \frac{\partial u}{\partial y} \right|_{y=0}^{\text{air}}, \text{ and since } \frac{\mu_{\text{air}}}{\mu_{\text{water}}} \doteq \frac{1}{60},$$

and unless  $\left. \frac{\partial u}{\partial y} \right|_{y=0}^{\text{air}}$  is large, find  $\left. \frac{\partial u}{\partial y} \right|_{y=0}^{\text{water}} \doteq 0$

For a general, non-planar interface,



$$\tau_{xy}^0 = \mu \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) \Big|_{y=0} \quad (\text{where the second term is usually much smaller than the first, and becomes zero if planar})$$

and the usual BC on a liquid is taken to be:  $\tau_{xy}^0 \doteq 0$

We say that the surface is "stress-free" (free of tangential stress; if curved however, it can have normal stress due to capillarity)

But if Surfactant monolayer is Present,  $\mu \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \neq 0$ .

Also true for non-isothermal interfaces, with or without Surfactant Present (move on this later, when we discuss stability)

For a Newtonian interface, the tangential component of Stress is described by the "Boussinesq-Scriven" surface model which is the constitutive relation for the interface. Once coupled to bulk fluid, it provides the BC for Navier-Stokes eqn. at a free surface:

$$\mu \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \Big|_{y=0} = \frac{\partial \sigma}{\partial x} + \frac{\partial}{\partial x} \left( (\mu^s + K^s) \frac{\partial u^s}{\partial x} \right) \quad \text{----- (1),}$$

Surface Velocity  
(for 2D flow)

Where  $\mu$  is the viscosity of the liquid,  $\sigma$  is the surface tension and is a function of  $x$  and  $t$ , since different amount of surfactant can exist at different locations and times (unless system is in static equilibrium).  $\mu^s$  is called "Surface (excess)

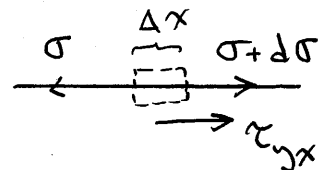
Shear Viscosity" and is the counter-part of  $\mu$ .  $K^s$  is called "Surface dilatational viscosity" and is the interfacial counter-part of "bulk"

viscosity. (Recall  $\mu_B = \lambda + \frac{2}{3}\mu$ , which according to Stokes hypothesis is zero, but is identically zero only for monatomic gases. But because it is the coefficient of the  $\text{div } \vec{V}$  term, unless change in volume is very rapid, e.g. a high Mach number shock wave, we tend to ignore  $\mu_B$  in much of fluid mechanics.)

( $\mu_B$  not to be confused with "viscosity in the bulk"  $\mu$ )

For a flat interface ( $v=0$  at  $y=0$ ), Eqn. 1 becomes:

$$\mu \left. \frac{\partial u}{\partial y} \right|_{y=0} = \frac{\partial \sigma}{\partial x} + \frac{\partial}{\partial x} \left( (\mu^s + \kappa^s) \frac{\partial u^s}{\partial x} \right) \quad \text{--- (2)}$$



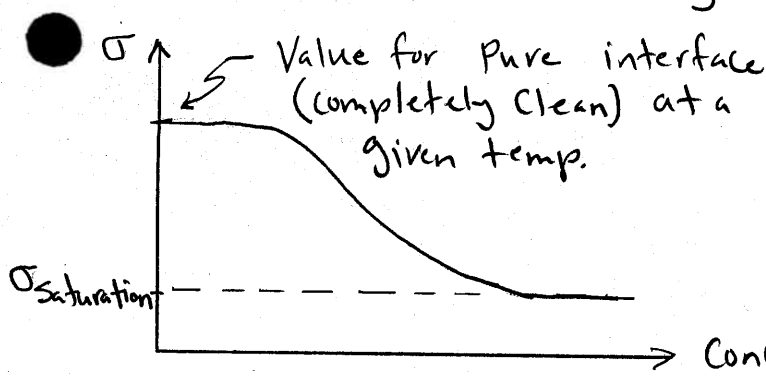
Shear stress on element due to shearing in the bulk (would be zero if liquid was inviscid). We've ignored viscosity on gas-side

Surface tension gradient (would be zero if surface tension was uniform)

Viscous dissipation due to motion along the interface (would be zero if surface did not have excess viscosity or in quasi-static compression; see Vogel & Hirs 02)

Linearize about some point:  $\mu \left. \frac{\partial u}{\partial y} \right|_{y=0} = \frac{\partial \sigma}{\partial x} + (\kappa^s + \mu^s) \frac{\partial^2 u^s}{\partial x^2}$

(We've studied the term on LHS extensively. Let us consider the other two terms)  $\sigma$  may nonuniform if surfactants are present:

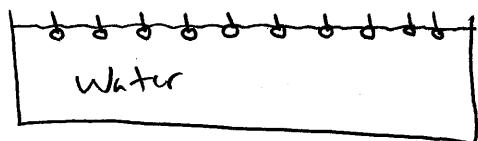


"Equation of State" of the Surface (aka "equilibrium isotherm") due to its similarity to eqn. of state for a gas,  $P(V)$  at a given  $T$

See VoH:02 for insoluble monolayer (T.P.)  
"Adamson" Soluble (T.P.)

(Note that, generally, surfactants reduce the surface tension from its clean value). This makes the interface elastic:

example air



Initially uniform film

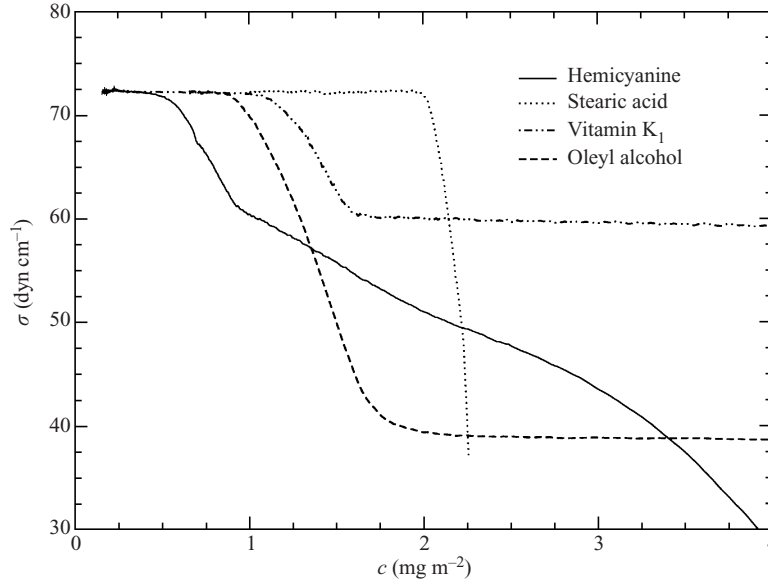


FIGURE 9. Equations of state measured for the four insoluble surfactants (concentration error:  $\pm 2.5\%$ ; surface tension error:  $\pm 0.1 \text{ dyn cm}^{-1}$ ).

stearic acid was not repeatable. However, the concentrations encountered in this study were all in the measured range.

A curve fit was found for the measured shear stress for various free-stream velocities (independent of the monolayer material). As shown in figure 5(b), the measured shear is similar to the Blasius solution for  $x < 6 \text{ cm}$  but larger for  $x > 6 \text{ cm}$ . Figure 10(a) shows the fit for the experimental data as well as the Blasius solution, both for  $U_\infty = 18 \text{ cm s}^{-1}$ . The model that was used in fitting the shear data blends a linear profile for low values of  $x$  with a modified Blasius solution at higher values of  $x$ . This is better than the Blasius solution because it avoids the singularity at the origin (Carrier & Lin 1948; Harper & Dixon 1974; Harper 1992). Due to the deviations between the measured shear and the Blasius solution, the curve fit for the shear stress at the interface includes an arbitrary shape factor,  $A(x)$ , for the Blasius term:

$$\mu \left. \frac{\partial u}{\partial y} \right|_{y=0} = \tau_F = \frac{1}{(1/\tau_L) + (1/\tau_B)A(x)}. \quad (4.5)$$

This fit for the shear stress at the interface,  $\tau_F$ , has the form of the lens equation which has been suggested for many different applications (Coles 1996). The linear portion of the curve fit, which is dominant at low values of  $x$ , is  $\tau_L = \mu G x \sqrt{U_\infty}$ ; the Blasius solution is  $\tau_B = \alpha \mu U_\infty^{3/2} / \sqrt{\nu x}$  where  $\alpha$  is the constant from the Blasius solution (0.332); and the shape factor is  $A(x) = x^{0.685} / (0.65 + 0.5x)$ . Here,  $\mu$  and  $\nu$  are respectively the dynamic and kinematic viscosities of the bulk fluid and  $G$  ( $= 325$ ) determines the magnitude of the peak shear. Note that all dimensional quantities are in c.g.s. units. The maximum uncertainty in BFDPIV measurements due to the finite resolution of the probe occurs at the monolayer front where the gradients are largest. The effect of changing the peak shear by  $\pm 25\%$  (by varying  $G$  from 504 to 183) is shown by the shaded region in figure 10(a).

The results of the concentration profile calculations using equation (4.4) with

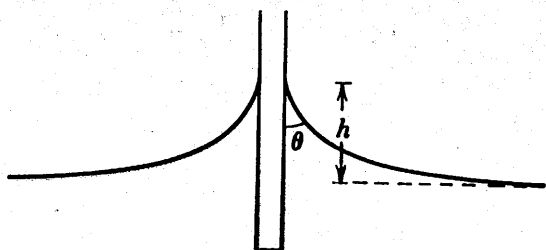


Fig. II-17. Meniscus profile for a nonwetting liquid.

where  $\Delta W$  is the change in weight of (i.e., force exerted by) the plate when it is brought into contact with the liquid, and  $p$  is the perimeter of the plate. The contact angle, if finite, may be measured in the same experiment (49). Integration of Eq. II-12 gives

$$\left(\frac{h}{a}\right)^2 = 1 - \sin \theta \quad (\text{II-28})$$

where, as illustrated in Fig. II-17,  $h$  is the height of the top of the meniscus above the level liquid surface. Zero contact angle is preferred, however, if only the liquid surface tension is of interest; it may help to slightly roughen the plate, see Refs. 41 and 50.

As an example of the application of the method, Neumann and Tanner (49) followed the variation with time of the surface tension of aqueous sodium dodecyl sulfate solutions. Their results are shown in Fig. II-18, and it is seen that a slow but considerable change occurred.

A modification of the foregoing procedure is to suspend the plate so that it is partly immersed and to determine from the dry and immersed weights the

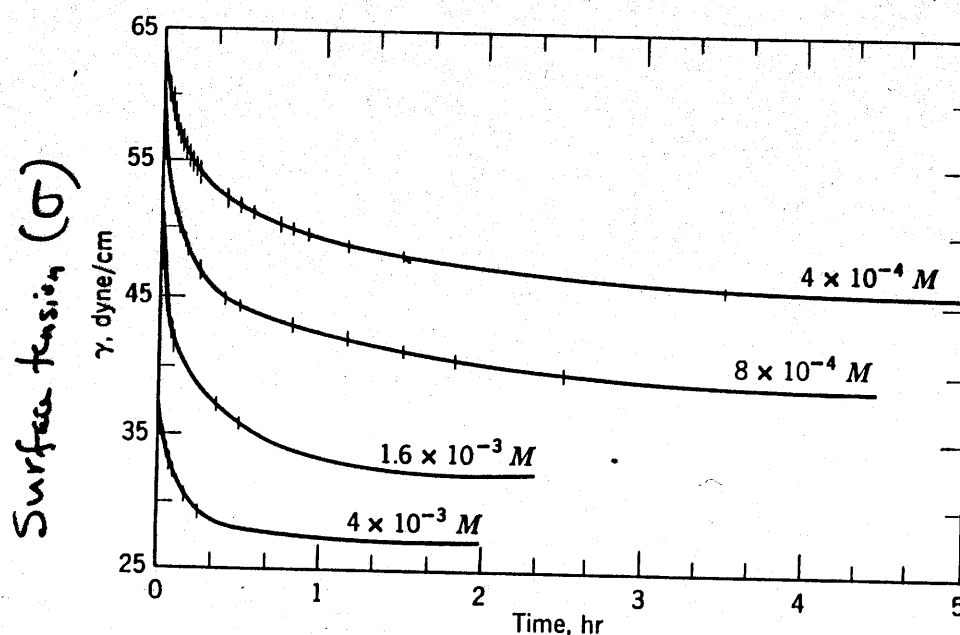
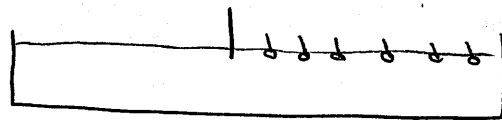


Fig. II-18. Variation with time of aqueous sodium dodecyl sulfate solutions of various concentrations (from Ref. 51). See Ref. 51 for later data with highly purified materials.

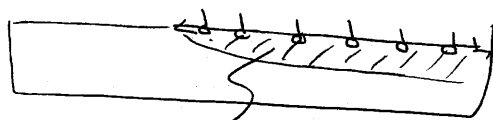
From: Adamson Physical Chemistry of Surfaces  
(1991)

Also, if we start with:



and the fluid at rest, then

if we remove the barrier, not only does the film travel to the left, but it will drag bulk fluid with it due to the coupling between the interface and the bulk as expressed by (1) and (2).



This flow is called "Marangoni Convection" boundary layer.  
(more on this later)

The viscous terms act in a similar manner to the elastic

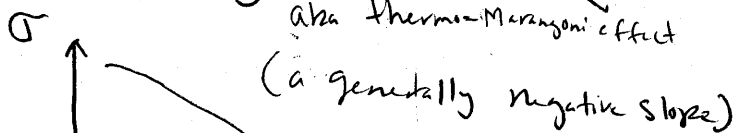
term against the viscous stress on the substrate; and we say that an interface covered by surface films is "viscoelastic". although both fluid & interface exert Newtonian

Note that since  $\sigma$  is relatively straight forward to measure, the elastic term can be isolated relatively easily by

keeping track of the advection of the film,  $C(x,t)$

However, unlike  $\sigma$ ,  $\mu^s$  and  $K^s$  (especially  $K^s$ ) are very difficult to measure and are subject of intense research.

Also note that surface tension gradients may exist at an uncontaminated <sup>(rare!)</sup> interface if temperature gradients exist on the surface, since  $\sigma = \sigma(T)$ . This is the mechanism for "thermo-capillary" convection. (We'll study these in stability analysis)



(this can be an important mechanism in areas ranging from material processing to propagation of a flame on surface of liquid fuel)

(Above discussion suggests that the mechanism for wave damping due to surface dissipation acts by generating an oscillatory free-surface boundary layer due to the change in surfactant concentration associated with the wave motion. Thus, the wave dampening due to surface dissipation may be significantly larger than the internal dissipation which occurs because viscous stresses must decrease from their bulk value to zero at the interface.)

Video on surface tension

(first Trefethen's, then Langmuir)  
(30 minutes) (35 min.)

an example of this: Vo Hi '02 JFM  
this (viscoelastic) model