

flow phenomena, known as *Marangoni effects*.^{9,10}

- (a) Verify the dimensional consistency of each interfacial balance equation.
 (b) Under what conditions are \mathbf{v}^I and \mathbf{v}^{II} equal?
 (c) Show how the balance equations simplify when phases I and II are two pure immiscible liquids.
 (d) Show how the balance equations simplify when one phase is a solid.

11C.7. Effect of surface-tension gradients on a falling film.

(a) Repeat the determination of the shear-stress and velocity distributions of Example 2.1-1 in the presence of a small temperature gradient dT/dz in the direction of flow. Assume that this temperature gradient produces a constant surface-tension gradient $d\sigma/dz = A$ but has no other effect on the physical properties. Note that this surface-tension gradient will produce a shear stress at the free surface of the film (see Problem 11C.6) and, hence, will require a nonzero velocity gradient there. Once again, postulate a stable, nonrippling, laminar film.

(b) Calculate the film thickness as a function of the net downward flow rate and discuss the physical significance of the result.

$$\text{Answer: (a) } \tau_{xz} = \rho g x \cos \beta + A; v_z = \frac{\rho g \delta^2 \cos \beta}{2\mu} \left[1 - \left(\frac{x}{\delta} \right)^2 \right] + \frac{A\delta}{\mu} \left(1 - \frac{x}{\delta} \right)$$

11D.1. Equation of change for entropy. This problem is an introduction to the thermodynamics of irreversible processes. A treatment of multicomponent mixtures is given in §§24.1 and 2.

(a) Write an entropy balance for the fixed volume element $\Delta x \Delta y \Delta z$. Let \mathbf{s} be the *entropy flux vector*, measured with respect to the fluid velocity vector \mathbf{v} . Further, let the *rate of entropy production* per unit volume be designated by g_s . Show that when the volume element $\Delta x \Delta y \Delta z$ is allowed to become vanishingly small, one finally obtains an *equation of change for entropy* in either of the following two forms:¹¹

$$\frac{\partial}{\partial t} \rho \hat{S} = -(\nabla \cdot \rho \hat{S} \mathbf{v}) - (\nabla \cdot \mathbf{s}) + g_s \quad (11D.1-1)$$

$$\rho \frac{D\hat{S}}{Dt} = -(\nabla \cdot \mathbf{s}) + g_s \quad (11D.1-2)$$

in which \hat{S} is the entropy per unit mass.

(b) If one assumes that the thermodynamic quantities can be defined locally in a nonequilibrium situation, then \hat{U} can be related to \hat{S} and \hat{V} according to the thermodynamic relation $d\hat{U} = Td\hat{S} - p d\hat{V}$. Combine this relation with Eq. 11.2-2 to get

$$\rho \frac{D\hat{S}}{Dt} = -\frac{1}{T} (\nabla \cdot \mathbf{q}) - \frac{1}{T} (\boldsymbol{\tau} : \nabla \mathbf{v}) \quad (11D.1-3)$$

(c) The local entropy flux is equal to the local energy flux divided by the local temperature¹²⁻¹⁵; that is, $\mathbf{s} = \mathbf{q}/T$. Once this relation between \mathbf{s} and \mathbf{q} is recognized, we can compare Eqs. 11D.1-2 and 3 to get the following expression for the rate of entropy production per unit volume:

¹¹ G. A. J. Jaumann, *Sitzungsber. der Math.-Naturwiss. Klasse der Kaiserlichen Akad. der Wissenschaften (Wien)*, **102**, Abt. IIa, 385–530 (1911).

¹² **Carl Henry Eckart** (1902–1973), vice-chancellor of the University of California at San Diego (1965–1969), made fundamental contributions to quantum mechanics, geophysical hydrodynamics, and the thermodynamics of irreversible processes; his key contributions to **transport phenomena** are in C. H. Eckart, *Phys. Rev.*, **58**, 267–268, 269–275 (1940).

¹³ C. F. Curtiss and J. O. Hirschfelder, *J. Chem. Phys.*, **18**, 171–173 (1950).

¹⁴ J. G. Kirkwood and B. L. Crawford, Jr., *J. Phys. Chem.*, **56**, 1048–1051 (1952).

¹⁵ S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland, Amsterdam (1962).