LETTERS TO THE EDITOR

To the Editor:

The recent article by Slattery (1977) presents an excellent, rigorous derivation to obtain stability criteria for multicomponent, multiphase systems [Eqs. (73) or (74) and Eqs. (75 or (76)]. It is, however, interesting to note that these same criteria can also be readily obtained from Legendre transform theory.

Eqs. (73) or (74) (in Slattery's paper) have, in fact, already been given (Beegle et al., 1974) in a slightly different form, i.e., in the latter's Eq. (21). To illustrate, consider a ternary system of A, B, C. Beegle et al. present a table (Table 3) showing alternate formulations of the stability criterion. If, for example, the A_{cc}'' form is selected,

$$\begin{aligned} A_{cc}'' &= (\partial\mu_c/\partial N_c)_{T,\mu_A,\mu_B,\underline{V}} > 0 \\ &= (1/V)[\partial\mu_c/\partial(N_c/\underline{V})]_{T,\mu_A,\mu_B,\underline{V}} \\ &= (1/\underline{V})(\partial\mu_c/\partial\rho_c)_{T,\mu_A,\mu_B} > 0 \end{aligned}$$

which is equivalent to the first form of Eq. (73) from Slattery. His other forms may be obtained in a similar manner, e.g., Eq. (74) is equivalent to the U_{SS}''' form in Beegle et al.

Slattery's interfacial criterion, Eq. (75) can also be derived from Legendre transforms and Eq. (21) of Beegle et al. The total internal energy of the surface phase is expressed as

$$\underset{\sim}{U} = U(\underset{\sim}{S}, N_1, N_2, \ldots, N_{n-1}, s, N_n) \qquad (1)$$

where s is the area and N_i refers to the moles of i in the surface phase. Examining this surface phase as an isolated system, the criterion of stability from Beegle et al. [Eq. (22)] is,

$$(\partial\xi_{n+1}/\partial x_{n+1})_{\xi_1,\xi_2,\ldots\xi_n,x_{n+2}} > 0 \qquad (2)$$

where

$$\xi_j = (\partial \underset{\sim}{U}/\partial x_j)_{x_i(i\neq j)} \qquad (3)$$

Note the ordering was carefully chosen in Eq. (1) so that

$$\xi_{n+1} = (\partial \underset{\sim}{U}/\partial s)_{\underset{\sim}{S},N_1,\ldots N_n} = \gamma \qquad (4)$$

with γ the interfacial tension. Eq. (2) then becomes

$$(\partial\gamma/\partial s)_{T,\mu_1,\ldots,\mu_{n-1},N_n} > 0 \qquad (5)$$

But, with N_n constant, $\rho_n = N_n/s$ and

$$ds = -(s^2/N_n)d\rho_n \qquad (6)$$

so Eq. (5) becomes

$$-(\partial\gamma/\partial\rho_n)_{T,\mu_1,\mu_2,\ldots,\mu_{n-1}} > 0 \qquad (7)$$

(neglecting any positive multipliers). This result is equivalent to Eq. (75) of Slattery.

BRUCE L. BEEGLE
ROBERT C. REID
Department of Chemical Engineering
Massachusetts Institute of Technology.

NOTATION

See Beegle et al. (1974).

LITERATURE CITED

Beegle, B. L., M. Modell, and R. C. Reid, "Thermodynamic Stability Criterion for Pure Substances and Mixtures," *AIChE J.* 20, 1200 (1974).

Slattery, J. C., "Limiting Criteria for Intrinsically Stable Equilibrium in Multiphase, Multicomponent Systems," *AIChE J.*, 23, 275 (1977).

Reply:

I am pleased Beegle and Reid have pointed out that the results for intrinsic stability of a multiphase system can be obtained by a simple extension of their previous reasoning.

It is especially interesting since they require the interface to be isolated. This probably could not be achieved experimentally. It is also somewhat more restrictive than my assumption that mass transfer could be neglected in a limit of sufficiently small random transients (Equation 49) but that free interchange of momentum, energy, and entropy between the interface and the adjoining phases was permitted.

J. C. SLATTERY
Department of Chemical Engineering
Northwestern University

To the Editor:

In a recent paper Ramabhadran *et al.* (1976) present some calculations concerning the rate at which oscillations die out in a fluid drop which has been deformed slightly from its initial spherical configuration. Among other things, they conclude that when surfactant is present at the interface, it is most effective in damping oscillations of a liquid drop in air when it produces large values of interfacial *dilational* elasticity. But surfactant damps oscillations of a bubble or cavity most effectively when it produces large values of interfacial *shear* elasticity.

The authors give no direct comparison of calculated damping rates due to dilational and shear effects for a particular drop or bubble to support these conclusions. In fact, as is shown below, the conclusions are not valid for some important situations of interest. Moreover, it appears that the contrary is true for a rather wide range of conditions, i.e., resistance to shear is most effective in damping oscillations of a drop and resistance to expansion and compression is most effective in damping oscillations of a cavity.

A general analysis of small oscillations of a fluid drop immersed in an immiscible fluid has been given by Miller and Scriven (1968), hereafter referred to as MS. This analysis was used by Ramabhadran *et al.* (1976) as the basis for their calculations except that, in dealing with cavities, they were careful to express the effect of interfacial viscosities and *elasticities* in terms of the velocity distribution in the liquid outside the cavity. This procedure assures that neglecting motion of the vapor within the cavity introduces no error.

The same approach is used here except that the dispersion equation describing drop behavior is expanded asymptotically to obtain equations which are valid when viscosities of both interior and exterior fluids are low. This method was also used by MS, who showed it to be a good approximation when fluid viscosities are a few centipoise or less and when drop size is not too small.

Whenever interfacial dilational elasticity and/or viscosity are very large (with interfacial shear elasticity and viscosity remaining moderate), the expansion leads to the following results obtained by MS:

Liquid drop in air

$$\beta_D = \frac{\sqrt{\beta^*_D \nu_D}\,(l-1)^2}{2\sqrt{2}R(l+1)} \qquad (1)$$

Cavity in a large expanse of liquid

$$\beta_C = \frac{\sqrt{\beta^*_C \nu_C}\,(l+2)^2}{2\sqrt{2}Rl} \qquad (2)$$

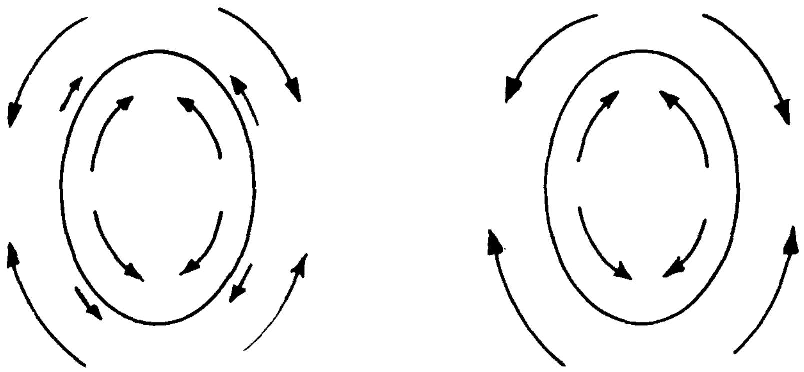
Here β_D and β_C are the damping parameters for the two cases with oscillation amplitude varying as $e^{-\beta t}$. Also β_D^* and β_C^* are the respective oscillation frequencies in the absence of viscous effects, ν_D and ν_C are the kinematic viscosities of the drop and of the liquid in which the cavity resides, R is the drop or cavity radius, and l is the mode number of the deformation. The mode damped most slowly is that for $l = 2$, which corresponds to deformation into a shape which is approximately ellipsoidal. Equation (2) for the cavity has also been derived using the extra precaution against error mentioned above.

If, in contrast, interfacial shear elasticity and/or viscosity are very large with interfacial dilational elasticity and viscosity remaining moderate, expansion of the dispersion equation gives the following new results:

Liquid drop in air

$$\beta_D = \frac{\sqrt{\beta^*_D \nu_D}}{2\sqrt{2R}}\,(l+1) \qquad (3)$$

Cavity in a large expanse of liquid



(a) (b)

Fig. 1. Flow pattern near a drop or cavity as it becomes more ellipsoidal during an oscillation. (a) Large dilational elasticity or viscosity. (b) Large shear elasticity or viscosity.

$$\beta_C = \frac{\sqrt{\beta^*_C \nu_C}}{2\sqrt{2}R}\,l \qquad (4)$$

Liquid-liquid situation

$$\beta_C = \frac{\sqrt{\beta^*}\,(\sqrt{\mu_o\rho_o}\,l^2 + \sqrt{\mu_i\rho_i}\,(l+1)^2)}{2\sqrt{2}\,R(\rho_o l + \rho_i(l+1))} \qquad (5)$$

In the last equation μ and ρ represent fluid viscosity and density, while the subscripts i and o denote the interior and exterior liquids, respectively. The cavity result (4) has again been verified independently.

For the mode $l = 2$ Equations (1) and (3) show that oscillations of a drop are damped nine times more strongly by shear effects than by dilational effects. On the other hand, Equations (2) and (4) imply that oscillations of a cavity are damped four times more strongly by dilational than by shear effects. With the additional information that, for given fluid properties and given radius, the oscillation frequency β^* is slightly greater for a cavity than for a drop (see MS), Equations (3) and (4) show that shear effects produce about equal damping rates in drop and cavity.

These results can be understood from the flow patterns shown in Figure 1. At a time during the oscillation when the drop or cavity is becoming more ellipsoidal and less spherical, the tangential velocity far from the interface has the patterns shown in the interior and exterior fluids. But tangential flow at the interface depends on interfacial rheological properties. When interfacial dilational elasticity and/or viscosity are large, flow along the interface occurs as shown in (a) to minimize local expansion and compression effects. When resistance to shear (but not dilation) is large, relatively little tangential flow occurs at the interface as in (b). If resistances to *both* dilation and shear are very large, no oscillation can occur (see MS).

As discussed by MS, the rate of damping in all these situations is determined by the rate of viscous dissipation in an oscillating boundary layer near the interface. The greater the difference in tangential velocity between the interface and bulk fluid, the greater the rate at which oscillations are damped. Figure 1 shows that when resistance to local expansion is large, the tangential velocity difference is greater for a cavity than for a drop, and indeed Equations (1) and (2) predict a much greater damping rate for the cavity. When resistance to local shear is large, tangential velocity at the interface is small and damping rates should be about the same for drop and cavity, in agreement with predictions of Equations (3) and (4). For a drop, Figure 1 indicates that the velocity difference between interface and bulk fluid is greater when shear resistance dominates. As expected, Equation (3) shows that damping is greater in this case as well. For a cavity the velocity difference is greatest when dilational resistance dominates, and again the analysis correctly predicts a higher damping rate for this situation.

CLARENCE A. MILLER
Department of Chemical Engineering
Carnegie-Mellon University

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Miller, C. A. and L. E. Scriven, "The Oscillations of a Fluid Droplet Immersed in Another Fluid," *J. Fluid Mech.*, **32**, 417 (1968).