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Wave motion of low-tension interfaces with electrical double layers

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An approximate solution is developed for the system of equations describing flow and ion transport in a diffuse electrical double layer slightly perturbed from equilibrium. The approximation is valid only when the potential difference across the diffuse layer is small, less than about 25 mV. When the approximate solution is used to study wave motion of low-tension interfaces, it is found that ion transport in diffuse layers slows down interfacial motion in both stable and unstable situations. Although the slowing effect is relatively small (a few per cent or less) when the small potential approximation applies, the form of the solution suggests that the effect could be significant for potential differences in the 50–100 mV range, which exist in many systems of interest. There are also indications that the slowing effect can significantly influence wave motion of thin liquid films with diffuse layers, e.g. soap films, although a detailed analysis of the thin-film situation is not carried out.

1. Introduction

Interfaces of low tension, i.e. a few dynes per centimetre or less, occur in oil–water systems when certain surfactants are present, in many biological systems and in fluids near critical or critical solution points. Tensions down to about 0·001 dyne/cm have been observed (for further discussion and references see Miller & Scriven 1970*a*). Understanding the wave motion of low-tension interfaces is important because, by their very nature, they are much easier to deform than more familiar interfaces of higher tension. As a result, small vibrations, perhaps even random thermal motion, can initiate wave motion of significant amplitude.

When interfacial tension is low its contribution to the energy of interfacial deformation is small. Consequently, other effects which also make small contributions may be quite important in low-tension systems, even though they have no appreciable influence on wave motion of ordinary high-tension interfaces. One such effect, the one of interest here, is that of electrical forces in double layers.

As might be expected, the smallness of interfacial tension's stabilizing influence makes low-tension interfaces subject to instability. Miller & Scriven (1970*b*) presented a thermostatic stability analysis for low-tension interfaces having diffuse double layers of the Gouy–Chapman type (Verwey & Overbeek 1948). One assumption of the thermostatic analysis is that a diffuse layer offers no resistance to the transport of ions, i.e. ionic diffusion coefficients are effectively infinite. The stability condition is not affected by this assumption because at marginal stability there is no motion of the interface and no driving force for ion diffusion. However, when the interface does move, either during stable wave motion or during the growth of an unstable disturbance, electrochemical potential gradients do occur and the thermostatic assumption may no longer be adequate.

This paper assesses the dynamic effects of ion transport on wave motion of low-tension interfaces with diffuse layers. To solve the general equations describing flow and ion transport in a diffuse layer would be a formidable task. It is not undertaken here. Instead an approximate solution from which useful information can be extracted and promising areas for further research identified is sought. When the potential drop across the diffuse layer is small – less than about 25 mV – the equations can be simplified considerably because, as is shown below, the total ion concentration becomes independent of position and the momentum equation reduces to the same form as that found when no electrical effects are present. With these simplifications an approximate solution can be obtained using the procedure described below.

The approximate solution indicates that ion transport acts to slow down interfacial motion, reducing the oscillation frequency when the interface is stable and the disturbance growth rate when it is unstable. These effects are due to retarding electrical forces which arise when a finite resistance to ion transport exists. Although the slowing effect is relatively small, being no larger than a few per cent for the small potential drops to which the approximation applies, the form of the solution suggests that the effect could be much larger when potential drops are in the range of 50–100 mV, which is representative of many systems of interest. Thus, ion transport in diffuse layers should be considered in interpreting capillary wave phenomena and related movements of low-tension interfaces with double layers. The results also suggest that ion transport may be an important factor influencing wave motion of thin liquid films of low tension, but confirmation of this possibility awaits further research.

The analysis of this paper is related to existing electrohydrodynamic treatments which show how applied electric fields influence interfacial stability and wave motion in systems having neither ions nor double layers (Melcher 1963; Melcher & Smith 1969). Indeed, the present work may be viewed as one step in the development of electrohydrodynamic theory for systems with double layers. This matter is discussed further below.

2. Plane diffuse layer before deformation

The system considered is a dilute incompressible solution of a single salt which dissociates into positive and negative ions of equal valence ν_0. If the solution has a uniform dielectric constant ϵ, the governing differential equations for flow and transport are as follows.

Momentum (Newtonian fluid):

$$\rho\, d\mathbf{v}/dt = -\nabla p + \mu\nabla^2\mathbf{v} + \rho_e\mathbf{E}. \tag{1}$$

Continuity:

$$\nabla \cdot \mathbf{v} = 0. \tag{2}$$

Equations of electric field (usual electrostatic approximation of Maxwell's equations; see Penfield & Haus 1967):

$$\nabla \times \mathbf{E} = 0 \quad \text{or} \quad \mathbf{E} = -\nabla \Psi, \tag{3}$$

$$\nabla^2 u = (-4\pi \nu_0 e_0/\epsilon kT)\rho_e. \tag{4}$$

Conservation of individual species (dilute ideal solution; see Bird *et al.* 1960):

$$dc_+/dt = \mathscr{D}_+ \nabla . (\nabla c_+ + c_+ \nabla u), \tag{5}$$

$$dc_-/dt = \mathscr{D}_- \nabla . (\nabla c_- - c_- \nabla u). \tag{6}$$

In these equations the free charge density and dimensionless electrical potential are defined by

$$\rho_e = \nu_0 e_0 N_0 (c_+ - c_-), \tag{7}$$

$$u = \nu_0 e_0 \Psi/kT. \tag{8}$$

Also, $\mathscr{D}_+$ and $\mathscr{D}_-$ are diffusion coefficients, N_0 is Avogadro's number, e_0 the magnitude of the electronic charge, k the Boltzmann constant, T the absolute temperature and $\mathbf{E}$ the electric field. In connexion with (1), it should be noted that the entire electrical body force can be expressed in the following form (Sanfeld 1968):

$$\rho_e \mathbf{E} - \frac{E^2}{8\pi}\nabla\epsilon + \nabla\left[\frac{E^2}{8\pi}\rho\left(\frac{\partial\epsilon}{\partial\rho}\right)_T\right]. \tag{9}$$

The second term of (9) vanishes here since ϵ is taken as uniform, while the third term has, for convenience, been included in the pressure p, i.e.

$$p = p_{\text{mech}} - (E^2/8\pi)\rho(\partial\epsilon/\partial\rho)_T,$$

where p_{mech} is the usual mechanical pressure.

For an interface with a diffuse layer in which there is no convection and no net flux of either ion at any point, (4)–(6) may be combined to obtain the well-known Poisson–Boltzmann equation:

$$\nabla^2 u = \kappa^2 \sinh u. \tag{10}$$

In this equation κ^{-1} is the Debye length, a measure of diffuse-layer thickness, and is defined by

$$\kappa^{-1} = (\epsilon kT/8\pi\nu_0^2 e_0^2 N_0 c_0)^{\frac{1}{2}}, \tag{11}$$

where c_0 is the concentration of each ion in the bulk solution outside the diffuse-layer region. Equation (10) can be solved exactly to obtain the potential distribution in an equilibrium diffuse layer near a plane interface (Verwey & Overbeek 1948) or near a plane interface which has been given a small wavy perturbation (Miller & Scriven 1970*a*). However, when ions in the diffuse layer are not in equilibrium after the interfacial deformation, which is the situation of interest here, the system of coupled differential equations is much more difficult to solve.

Considerable simplification of the equations occurs, however, when the dimensionless potential u is taken to be somewhat less than unity at all points, i.e. when the potential drop across the diffuse layer is less than about 25 mV. This approximation for small potentials, frequently called the Debye–Hückel approximation, is discussed further below. When it is applied to a plane diffuse layer in equilibrium (10) reduces to

$$d^2u/dz^2 = \kappa^2 u. \tag{12}$$

When (12) is solved for a diffuse layer in the region $z \geqslant 0$, it is found that the potential varies exponentially and that the concentration distributions are given by

$$c_+ = c_0 e^{-u} \cong c_0(1-u), \tag{13}$$

$$c_- = c_0 e^{u} \cong c_0(1+u). \tag{14}$$

Because u is small, terms of order u^2 are neglected. It is convenient to define two new quantities from (13) and (14) as follows:

$$\theta = c_+ + c_- \cong 2c_0, \tag{15}$$

$$\phi = c_+ - c_- = \rho_e/(\nu_0 e_0 N_0) \cong -2c_0 u. \tag{16}$$

Here θ is the total ion concentration, while ϕ is closely related to the free charge density.

3. Transport in diffuse layer during deformation

When the equilibrium diffuse layer described by (12)–(16) is given a small wavy perturbation its asymptotic behaviour can be determined by the well-known normal-mode method (see, for example, Chandrasekhar 1961). According to this method, the interfacial position z_I for the mode of wavenumber α is given by

$$z_I = Bf(x,y)\, e^{-\beta t}. \tag{17}$$

The function f of (17) describes the form of the perturbation; it is a periodic, e.g. sinusoidal, function of its arguments and satisfies the following equation:

$$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} = -\alpha^2 f. \tag{18}$$

Moreover, the normal velocity, electrical potential, and concentration distributions in the perturbed diffuse layer all have the form

$$F(x,y,z,t) = F_i(z) + F_p(z) f(x,y)\, e^{-\beta t}, \tag{19}$$

where the subscript i refers to values before interfacial deformation while the subscript p refers to perturbations produced by the deformation.

When appropriate fields of the form (19) are substituted into the governing differential equations and when only terms of first order in the perturbations are retained, the following set of coupled ordinary differential equations is obtained.

Normal component of vorticity equation:

$$(D^2 - \alpha^2 r^2) Z = 0. \tag{20}$$

Normal component of curl of vorticity equation:

$$(D^2 - \alpha^2)(D^2 - \alpha^2 r^2)\, W = (-\alpha^2 kTN_0 \kappa u_0 e^{-\kappa z}/\mu)(2c_0 u_p + \phi_p). \tag{21}$$

Equation of electric field:

$$(D^2-\alpha^2)\,u_p = (-\kappa^2/2c_0)\,\phi_p. \tag{22}$$

Sum of species equations (with $\mathscr{D}_+ = \mathscr{D}_- = \mathscr{D}$):

$$\left(D^2-\alpha^2+\frac{\beta}{\mathscr{D}}\right)\theta_p = \kappa u_0 e^{-\kappa z}(D-\kappa)\,\phi_p+2c_0u_0e^{-\kappa z}(D^2-\kappa D-\alpha^2)\,u_p. \tag{23}$$

Difference between species equations (with $\mathscr{D}_+ = \mathscr{D}_- = \mathscr{D}$):

$$\left(D^2-\alpha^2+\frac{\beta}{\mathscr{D}}\right)\phi_p+2c_0(D^2-\alpha^2)\,u_p-\kappa u_0e^{-\kappa z}(D-\kappa)\,\theta_p = \frac{2c_0\kappa u_0e^{-\kappa z}}{\mathscr{D}}\,W. \tag{24}$$

In these equations Z and W are normal components of vorticity and velocity (it is sometimes convenient in wave-motion analyses to work with Z instead of the tangential components of velocity; see Chandrasekhar 1961). Also u_0 is the (dimensionless) potential of the plane interface before deformation,

$$r^2 = 1-\beta\rho/\mu\alpha^2$$

and D is the operator $\partial/\partial z$. Now (22) can be used to eliminate ϕ_p from (21), (23) and (24), but three coupled differential equations in W, θ_p and u_p remain.

From (23) it can be seen that the perturbation θ_p in the total ion concentration has the form

$$\theta_p = \text{constant}\times\exp\{-[\alpha^2-(\beta/\mathscr{D})]^{\frac{1}{2}}z\}+\text{terms of order } u_0u_p. \tag{25}$$

The product u_0u_p is proportional to u_0^2; because the Debye–Hückel approximation applies terms in u_0u_p can be neglected here, just as terms proportional to u_0^2 were neglected in evaluating θ for the plane diffuse layer in (15). If it is assumed that there is no transfer of ions across the interface, the constant multiplying the first term of (25) is also of order u_0u_p, as can be seen by adding the ionic fluxes at the interface:

$$(j_++j_-)_{z_1} = -\mathscr{D}[D\theta_p-2c_0u_0e^{-\kappa z}\,Du_p-\kappa u_0e^{-\kappa z}\,\phi_p]_{z=0} = 0. \tag{26}$$

Thus, all terms in θ_p and its derivatives may be neglected.

The derivation has thus far been based on the assumption that ionic diffusion coefficients $\mathscr{D}_+$ and $\mathscr{D}_-$ are equal. However, once the relation $\theta_p \cong 0$, or $c_{+p} \cong -c_{-p}$, has been established, it can be used in combining the original species equations (5) and (6) to obtain (23) and (24) with $\mathscr{D}$ given by $2\mathscr{D}_+\mathscr{D}_-/(\mathscr{D}_++\mathscr{D}_-)$. This procedure should be valid provided that $\mathscr{D}_+$ and $\mathscr{D}_-$ differ only slightly, which is the usual situation.

When all terms in θ_p are neglected and when (22) is substituted into (21) and (24), these latter equations reduce to

$$(D^2-\alpha^2)\,(D^2-\alpha^2r^2)\,W = -\frac{\alpha^2\epsilon\kappa}{4\pi\mu}\left(\frac{kT}{\nu_0e_0}\right)^2u_0e^{-\kappa z}(D^2-\alpha^2-\kappa^2)\,u_p, \tag{27}$$

$$(D^2-\kappa^2h^2)\,(D^2-\alpha^2)\,u_p = -\frac{\kappa^3u_0e^{-\kappa z}}{\mathscr{D}}\,W. \tag{28}$$

Here h^2 is defined as $1+\alpha^2/\kappa^2-\beta/\mathscr{D}\kappa^2$. By eliminating W between (27) and (28) one obtains a single eighth-order ordinary differential equation that governs the behaviour of the perturbed diffuse layer:

$$\left(\bar{D}^2+2\bar{D}+1-\frac{\alpha^2}{\kappa^2}\right)\left(\bar{D}^2+2\bar{D}+1-\frac{\alpha^2 r^2}{\kappa^2}\right)(\bar{D}^2-h^2)\left(\bar{D}^2-\frac{\alpha^2}{\kappa^2}\right)u_p(\bar{z})$$

$$=\left[\frac{2\alpha^2\gamma_{DL}}{\mu\mathscr{D}\kappa^3}\right]e^{-2\bar{z}}\left(\bar{D}^2-\frac{\alpha^2}{\kappa^2}-1\right)u_p(\bar{z}). \quad (29)$$

In this equation $\bar{z}=\kappa z$, $\bar{D}=\partial/\partial\bar{z}$, and $\gamma_{DL}=\epsilon\kappa\Psi_0^2/8\pi$ is the magnitude of the diffuse layer's negative contribution to the interfacial tension (Verwey & Overbeek 1948). For a diffuse layer in a 0·001 molar aqueous solution of a univalent salt the Debye length κ^{-1} is about 10^{-6} cm (100 Å). When there is a potential drop of 22 mV across such a diffuse layer, γ_{DL} is about 0·02 dyne/cm. If the mean diffusion coefficient $\mathscr{D}$ has a value of $10^{-5}\,\mathrm{cm}^2/\mathrm{s}$ the dimensionless quantity in square brackets on the right-hand side of (29) is approximately equal to $4\times10^{-13}\alpha^2$ (α in cm^{-1}). This quantity is therefore very small when the wave-number α is less than about $10^5\,\mathrm{cm}^{-1}$, i.e. when the mean wavelength $(2\pi/\alpha)$ is greater than about 6×10^{-5} cm. Only wavelengths which satisfy this restriction and which are, as a result, much greater than the diffuse-layer thickness are considered here.

Neglecting the right-hand side of (29), solving for u_p and applying the condition that u_p must remain finite for large z, one finds that

$$u_p=A_1e^{-\kappa hz}+A_2e^{-\alpha z}+A_3e^{-(\alpha+\kappa)z}+A_4e^{-(\alpha r+\kappa)z}. \quad (30)$$

The normal velocity W can be obtained by combining (30) and (28) and is given by

$$W=-\frac{\mathscr{D}\kappa}{u_0}\left(1+2\frac{\alpha}{\kappa}\right)\left(2\frac{\alpha}{\kappa}+\frac{\beta}{\mathscr{D}\kappa^2}\right)A_3e^{-\alpha z}-\frac{\mathscr{D}\kappa}{u_0}\left[2\frac{\alpha r}{\kappa}+\frac{\alpha^2}{\kappa^2}(5r^2-1)+4\frac{\alpha^3}{\kappa^3}r(r^2-1)+\frac{\alpha^4}{\kappa^4}\right.$$

$$\left.+\frac{\beta}{\mathscr{D}\kappa^2}\left(1+2\frac{\alpha r}{\kappa}+\frac{\alpha^2}{\kappa^2}(r^2-1)\right)\right]A_4e^{-\alpha rz}. \quad (31)$$

It is noteworthy that this form of the velocity distribution, that is, a sum of terms proportional to $e^{-\alpha z}$ and $e^{-\alpha rz}$, is the same as that found using existing wave-motion analyses which consider no electrical effects (Chandrasekhar 1961). The reason is that neglecting the right-hand side of (29) amounts to neglecting all electrical terms in the differential equation for $W(z)$ obtained from the momentum equation.

The approximate solution given by (30) and (31) is closely related to that of Buck (1969), who considered the response of a diffuse layer to a step change in interfacial charge. The present analysis is, however, considerably more general than Buck's because it includes both convection and lateral variation of the potential and concentrations, effects which are unimportant for the situation Buck studied. It seems likely that the basic approach used here may also be useful in analysing other small perturbations of a diffuse layer from equilibrium, e.g. a diffuse layer through which a finite current flows.

4. Boundary conditions

Equations (30) and (31) give the normal velocity and electrical potential distributions for wave motion of a fluid with a diffuse layer in the region $z > z_I$. The constants $A_1 \dots A_4$ of these equations and A_5, arising in the solution of (20), must be determined by applying boundary conditions at $z = z_I$, the position of the wavy interface. Three additional constants arise when the usual hydrodynamic equations [(20) and (21) without electrical terms] are solved for the fluid in the region $z < z_I$, which is assumed to have no diffuse layer. As the interfacial displacement B is also unknown nine boundary conditions are required. Two of these conditions represent ion transport and electrical effects (see below for details). The remaining conditions are the usual ones of wave-motion analyses, viz. the kinematic condition (the rate of change of interfacial position must equal the normal component of velocity at the interface), continuity of velocity, and a balance of forces. Because these last two are vector conditions each leads to three scalar equations.

One boundary condition on ion transport, like (26) a consequence of the assumption that no ions cross the interface, is the zero current condition:

$$(j_+ - j_-)_{z_I} = -\mathscr{D}\left[\frac{\partial \phi}{\partial z} + \theta \frac{\partial u}{\partial z}\right]_{z_I} = 0. \tag{32}$$

When the results of the preceding section are substituted into (32), one finds that

$$[D^3 - (\alpha^2 + \kappa^2) D] u_p = 0 \quad \text{at} \quad z = 0. \tag{33}$$

When θ is approximately uniform, as in the present situation, the second term of (32) is directly proportional to the electric field. In other words, the conductivity is approximately uniform and Ohm's law describes this portion of the current when the Debye–Hückel approximation applies.

Another boundary condition involves the distribution of charge along the wavy interface. The interfacial charge may be due either to surface-active ions or to induced charge at the surface of a highly conducting fluid such as mercury. If the charge is mobile and can redistribute itself during deformation to eliminate tangential electric forces along the interface, as is certainly true for induced charge and may be true for ions, the interface remains at a uniform potential:

$$u_p(0) - u_0 \kappa B = 0. \tag{34}$$

Other boundary conditions are possible, but for simplicity they are not considered here. It has been shown elsewhere (Miller & Scriven 1970*a*) that, when the effects of ion transport are absent, the potential distribution is almost independent of the boundary condition provided that the wavelengths are much greater than the diffuse-layer thickness, which is true in the situation of interest here.

Because, as was noted previously, the form of the velocity distribution given by (31) is the same as that of the existing wave-motion analyses, the kinematic and velocity conditions of these analyses (Chandrasekhar 1961) can be taken over directly. So can the tangential component of the force balance since, with the constant potential condition (34), there are no tangential electrical forces, i.e. electrical shear stresses, at the interface.

The normal component of the force balance has, however, two terms of electrical origin. In the first place, normal electrical stresses act on the interface. The electrical portion of the stress tensor can be written in the following form (see Sanfeld 1968):

$$\tau_{\text{elec}} = \frac{\epsilon \mathbf{EE}}{4\pi} + \mathbf{U}\frac{E^2}{8\pi}\left[\rho\left(\frac{\partial \epsilon}{\partial \rho}\right)_T - \epsilon\right], \tag{35}$$

where $\mathbf{U}$ is the unit tensor. For the present situation the normal electrical stress at the interface is given by

$$(\tau_{\text{elec}})_{zz} = \frac{1}{8\pi}\left(\frac{kT}{\nu_0 e_0}\right)^2 \left\{\left(\frac{\partial u}{\partial z}\right)^2 \left[\epsilon + \rho\left(\frac{\partial \epsilon}{\partial \rho}\right)_T\right]\right\}_{z_I}. \tag{36}$$

Second, the electrical body force in the momentum equation (1) influences the pressure distribution. When the normal component and the divergence of the momentum equation are combined, the pressure distribution is found to have the form (19) with

$$\left.\begin{aligned} p_i(z) &= (p_{\text{mech}})_i - \frac{\rho}{8\pi}\left(\frac{\partial \epsilon}{\partial \rho}\right)_T \left(\frac{kT}{\nu_0 e_0}\right)^2 \left(\frac{\partial u_i}{\partial z}\right)^2 = p_b + \frac{\epsilon \kappa^2 u_i^2}{8\pi}\left(\frac{kT}{\nu_0 e_0}\right)^2, \\ p_p(z) &= (p_{\text{mech}})_p - \frac{\rho}{4\pi}\left(\frac{\partial \epsilon}{\partial \rho}\right)_T \left(\frac{kT}{\nu_0 e_0}\right)^2 \frac{\partial u_i}{\partial z}\frac{\partial u_p}{\partial z} = \frac{\epsilon \kappa^2 u_i u_p}{4\pi}\left(\frac{kT}{\nu_0 e_0}\right)^2 \\ &\qquad + (\text{hydrodynamic terms as in existing wave-motion analyses}). \end{aligned}\right\} \tag{37}$$

Here p_b is the pressure in the bulk solution outside the diffuse-layer region. When these two terms are included, the normal component of the interfacial force balance takes the form†

$$\begin{aligned} 0 = [p_{1p} - p_{2p} - 2\mu_1 DW_1 + 2\mu_2 DW_2]_{z=0} - B\left[\Delta\rho g + \gamma_p \alpha^2 - \frac{\epsilon \kappa^3 u_0^2}{4\pi}\left(\frac{kT}{\nu_0 e_0}\right)^2\right] \\ + \frac{\epsilon}{4\pi}\left(\frac{kT}{\nu_0 e_0}\right)^2 [Du_i(BD^2 u_i + Du_p)]_{z=0}. \end{aligned} \tag{38}$$

In this equation the subscript 2 refers to the fluid containing the diffuse layer, while the subscript 1 refers to the fluid with no double layer. Also, γ_p is the tension of the thin phase transition region separating the fluids, but excluding the much thicker diffuse-layer region (Miller & Scriven 1970*a*).

It is well known that normal electrical stresses as given by (36) can influence wave motion and even cause instability in systems where there are applied electric fields but no ions and therefore no double layers (Melcher 1963; Taylor

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† It can be shown that the electrically produced terms of the velocity distribution, which are small in comparison with the terms of (31) and are therefore omitted there, make a contribution to the normal force equation which is much smaller than that of the electrical stresses whenever $|\beta/\mathscr{D}\alpha\kappa| \ll 1$. Since the speed of interfacial motion and hence $|\beta|$ decreases with decreasing interfacial tension, this requirement can be met for sufficiently low values of the interfacial tension. Sections 5 and 6 below give further information on how low tension must be.

& McEwan 1965). However, in systems lacking double layers there is no counterpart of the electrical pressure terms given by (37). These terms plus, of course, the differential equations and boundary conditions describing ion transport differentiate the present work from existing electrohydrodynamic analyses of systems without double layers.

As was indicated previously, there is a total of nine scalar boundary conditions. Equations (33) and (34) can be used to eliminate A_1 and A_2 from the hydrodynamic boundary conditions, leaving seven linear homogeneous equations in seven unknowns. For a non-trivial solution to exist, the determinant of coefficients for this system of equations must vanish, a condition which yields, after some manipulation, the following dispersion equation:

$$\begin{vmatrix} \beta & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & -1 & 0 \\ 0 & r_2 & 1-r_2 & r_1 & 1-r_1 \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} \\ 0 & \mu_2(1+r_2^2) & \mu_2(1-r_2^2) & -\mu_1(1+r_1^2) & -\mu_1(1-r_1^2) \end{vmatrix} = 0. \qquad (39)$$

The constants C_{4i} of this equation are defined by

$$C_{41} = -\beta_p^{*2} + \frac{2\gamma_{DL}\kappa^2\alpha}{\rho_1+\rho_2}\left[\frac{h(1-y_D^2)}{1-(\kappa/\alpha)y_D^2} - 1\right],$$

$$C_{42} = \frac{\rho_2\beta r_2}{\rho_1+\rho_2}\left(1+\frac{r_2^2-3}{y_2^2}\right) - \frac{2\gamma_{DL}\kappa^2\alpha y_D^2}{(\rho_1+\rho_2)\beta}$$
$$\times\left[1+\frac{\alpha r_2}{\kappa} - \frac{h(1-y_D^2)+\left(h-\frac{\alpha}{\kappa}\right)\left(1+\frac{\alpha r_2}{\kappa}\right)\left(2r_2-\frac{\alpha}{\kappa}y_2^2\right)}{1-(\kappa/\alpha)hy_D^2}\right]$$
$$\times\left[\left(\frac{\alpha}{\kappa}\right)^4 y_2^4 - 4\left(\frac{\alpha}{\kappa}\right)^3 r_2 y_2^2 + \left(\frac{\alpha}{\kappa}\right)^2 (5r_2^2-1) + 2r_2\frac{\alpha}{\kappa} + y_D^2\left(1+2r_2\frac{\alpha}{\kappa} - y_2^2\left(\frac{\alpha}{\kappa}\right)^2\right)\right]^{-1},$$

$$C_{43} = \frac{\rho_2\beta}{\rho_1+\rho_2}\left(1-\frac{2}{y_2^2}\right) - \frac{2\gamma_{DL}\kappa^2\alpha y_D^2}{(\rho_1+\rho_2)\beta\left(1+2\frac{\alpha}{\kappa}\right)\left(2\frac{\alpha}{\kappa}+y_D^2\right)}$$
$$\times\left[1+\frac{\alpha}{\kappa} - \frac{h\left(3+2\frac{\alpha}{\kappa}-y_D^2\right)-2\frac{\alpha}{\kappa}\left(1+\frac{\alpha}{\kappa}\right)}{1-(\kappa/\alpha)hy_D^2}\right] - C_{42},$$

$$C_{44} = \frac{\rho_1\beta r_1}{\rho_1+\rho_2}\left(1+\frac{r_1^2-3}{y_1^2}\right), \quad C_{45} = \frac{\rho_1\beta}{\rho_1+\rho_2}\left(1-\frac{2}{y_1^2}\right) - C_{44}.$$

Also, $y_i^2 = \beta\rho_i/\mu_i\alpha^2$, $y_D^2 = \beta/\mathscr{D}\kappa^2$ and $\beta_p^* = [(\gamma_p\alpha^3+\Delta\rho g\alpha)/(\rho_1+\rho_2)]^{\frac{1}{2}}$, the frequency of wave motion in the absence of viscous and electrical effects.

5. Ion transport effect on wave motion

Equation (39) describes wave motion of interfaces with diffuse layers when the Debye–Hückel approximation applies. From it the time factor β of (17) and (19) can be calculated as a function of the wavenumber α, fluid and interfacial properties and electrical characteristics of the diffuse layer. For real α the time factor is in general a complex number. Its real part β_r specifies the rate of damping or growth of the disturbance; its imaginary part β_i specifies the angular frequency of oscillation. Another possibility, a more convenient one experimentally, involves imposing oscillations of a given frequency at a fixed location (Mann & Hansen 1963). In this case β is imaginary while α is complex, its real part corresponding to the wavenumber and its imaginary part indicating the rate of amplification or attenuation with distance from the source of oscillations.

Solution of (39) must in general be carried out numerically. It is possible, however, to simplify the determinant sufficiently to obtain some information about the effect of ion transport on wave motion. First of all, if the fluids have equal densities and viscosities, (39) reduces to

$$C_{41}(1-r)+\beta[rC_{45}-(1-r)C_{44}+rC_{43}-(1-r)C_{42}] = 0. \tag{40}$$

This simplification should not cause much error in systems where a light oil is in contact with water. Next, because the Debye length κ^{-1} can be quite small (about 100 Å), the time required for transport of an ion across the diffuse layer is normally much smaller than the characteristic time β^{-1} of the motion, i.e.

$$|y_D^2| = |\beta/\mathscr{D}\kappa^2| \ll 1.$$

Finally, when the time factor β is so small that $|r| = |(1-\beta\rho/\mu\alpha^2)^{\frac{1}{2}}|$ is of order unity or smaller, the coefficients C_{4i} can be expanded in powers of y_D^2 and α/κ, essentially the ratio of the diffuse-layer thickness to the wavelength. For aqueous diffuse layers with $\alpha/\kappa \leqslant 10^{-4}$, i.e. for relatively long wavelengths, the coefficients are given approximately by

$$C_{41} = -\beta_p^{*2}+\frac{\gamma_{DL}\kappa^3}{\rho^2}\frac{\mu}{\mathscr{D}}\frac{\alpha^2}{\kappa^2}(1-r^2)$$
$$\times\frac{\left[1-\frac{3}{2}\frac{\alpha}{\kappa}-\frac{1}{2}\frac{\mu a^2}{\rho\mathscr{D}\kappa^2}(1-r^2)+\frac{1}{2}\frac{\alpha}{\kappa}\frac{\mathscr{D}\rho}{\mu(1-r^2)}+\frac{1}{2}\frac{\alpha^2}{\kappa^2}+\dots\right]}{[1-(\kappa/\alpha)\,hy_D^2]}, \tag{41}$$

$$\beta C_{42} = \frac{\beta^2 r}{2}\left(1+\frac{r^2-3}{y^2}\right)+\frac{\gamma_{DL}\kappa^3}{\rho^2}\frac{\mu}{\mathscr{D}}\frac{\alpha^2}{\kappa^2}(1-r^2)$$
$$\times\frac{\left[1-\frac{\alpha}{\kappa}(r+\tfrac{3}{2})-\frac{1}{2}\frac{\mu\alpha^2}{\rho\mathscr{D}\kappa^2}(1-r^2)+(r^2+\tfrac{9}{4}r+\tfrac{3}{2})\frac{\alpha^2}{\kappa^2}+\dots\right]}{[1-(\kappa/\alpha)\,hy_D^2]}, \tag{42}$$

$$\beta C_{43} = \frac{\beta^2}{2}\left(1-\frac{2}{y^2}\right)+\frac{\gamma_{DL}\kappa^3}{\rho^2}\frac{\mu\alpha^2}{\mathscr{D}\kappa^2}(1-r^2)$$
$$\frac{\left[1-\frac{5}{2}\frac{\alpha}{\kappa}-\frac{1}{2}\frac{\mu\alpha^2}{\rho\mathscr{D}\kappa^2}(1-r^2)+\frac{19}{4}\frac{\alpha^2}{\kappa^2}+\dots\right]}{[1-(\kappa/\alpha)\,hy_D^2]}-\beta C_{42}. \tag{43}$$

The restriction to such small values of α/κ is required by the presence in the equations of the ratio $\mathscr{D}\rho/\mu$, which has a value of about 10^{-3} in aqueous systems. When the Debye length κ^{-1} is 100 Å (0·001 molar solution of a univalent salt), the expansions are valid for mean wavelengths greater than about 0·05 cm. Calculations show that for such wavelengths the above limitation on $|r|$ and the requirement $|\beta/(\mathscr{D}\kappa\alpha)| \ll 1$ (see footnote at (38)) are satisfied only when the total interfacial tension γ_T is less than about one dyne per centimetre. Hence the results obtained below apply only to low-tension interfaces.

When (41)–(43) are substituted into (40), the following equation is found after some rearrangement:

$$r^4+r^3(1+a_2)-r^2(1+\tfrac{1}{2}a_2)-r(1+a_2)+a_1+\tfrac{1}{2}a_2 = 0. \tag{44}$$

In this equation the constants a_1 and a_2 are defined by

$$a_1 = \beta_T^{*2}\rho^2/(\mu^2\alpha^4) = \gamma_T\rho/(2\mu^2\alpha), \quad a_2 = \gamma_{DL}/(\mu\mathscr{D}\kappa) = \epsilon\Psi_0'^2/(8\pi\mu\mathscr{D}). \tag{45}$$

Here β_T^{*2} is β_p^{*2} with the tension γ_p of the phase transition region alone replaced by the tension $\gamma_T = \gamma_p - \gamma_{DL}$ of the entire region between the bulk fluids, including the diffuse-layer region. For $\gamma_{DL} = 0$, (44) reduces to the corresponding dispersion equation in the absence of electrical effects (Chandrasekhar 1961). Similarly, for $\mathscr{D} \to \infty$ it reduces to the result found earlier for diffusion equilibrium when disturbances have long wavelengths, namely that the effect of the diffuse layer is simply a negative contribution to interfacial tension (Miller & Scriven 1970*b*).

Information on how ion transport influences wave motion can be obtained from (44). For a given value of a_1 the solutions r_u of (44) in the absence of double-layer effects, i.e. for $a_2 = 0$, can be readily calculated. The definition of r following (24) can then be used to calculate the corresponding time factors for the motion:

$$\beta_u = (\mu\alpha^2/\rho)(1-r_u^2). \tag{46}$$

Now if each solution r for the same a_1 and a small positive value of a_2 is written as the sum of an 'unperturbed' solution r_u and a small perturbation r_p, where $|r_p| \ll |r_u|$, it is easily shown from (44) that r_p is given by

$$r_p = -a_2\frac{r_u^3-\frac{1}{2}r_u^2-r_u+\frac{1}{2}}{4r_u^3+3r_u^2-2r_u-1}. \tag{47}$$

The corresponding perturbation in the time factor is

$$\beta_p = (-2\mu\alpha^2/\rho)\,r_u r_p. \tag{48}$$

For $a_1 = a_2 = 0$, (44) has the solution $r_u = 1$. (Only solutions with positive real parts are of interest since only then does the second exponential term of (31) remain finite as $z \to \infty$.) Hence, β_u vanishes and the interface is marginally stable. According to (47), the interface is also marginally stable when double-layer effects are present ($a_2 > 0$), provided that the total interfacial tension γ_T retains its zero value.

When a_1 is negative and a_2 is zero one finds that $r_u > 1$ and $\beta_u < 0$. The interface is thus unstable for negative values of the total interfacial tension. In this case

(47) and (48) predict a negative value for r_p and a positive value for β_p. The latter result implies that ion transport decreases the growth rate of unstable disturbances but does not remove the instability altogether.

When a_1 is positive, the situation is somewhat more complicated. For $0 < a_1 < 0{\cdot}62$ there are, for a given value of a_1, two positive real roots r_u, both lying between 0 and 1. The corresponding values of β_u are both real and positive, i.e. the interface is stable and returns aperiodically to the initial plane configuration. The root leading to the slower damping rate is of primary interest since it describes interfacial behaviour after motion associated with the other root has died out. For the more slowly damped root it can be shown that $0{\cdot}64 < r_u < 1$. According to (47) and (48), $r_p > 0$ and $\beta_p < 0$, so that in this case too ion transport acts to slow down interfacial motion.

For $a_1 > 0{\cdot}62$ there are two complex roots r_u which differ only in the signs of their imaginary parts. Both roots correspond to oscillatory motion with the same frequency and damping rate. For simplicity the following discussion is limited to the root with positive imaginary part although a similar argument leading to the same conclusion can be made for the other root. For the root of interest $r_u = r_{ur}+ir_{ui}$ with $r_{ui} > 0$, $r_{ur} > 0{\cdot}64$. Also $\beta_u = \beta_{ur}+i\beta_{ui}$ with $\beta_{ur} > 0$, $\beta_{ui} < 0$. If r_p is written as $r_{pr}+ir_{pi}$, (48) becomes

$$\beta_p \rho/\mu\alpha^2 = -2(r_{ur}r_{pr}-r_{ui}r_{pi})-2i(r_{ur}r_{pi}+r_{pr}r_{ui}). \tag{49}$$

Now it can be shown using (47) that $r_{pi} \leqslant 0$ for all r_u and that $r_{pr} < 0$ for all r_u having $r_{ur} > 1$. Under these conditions $\beta_{pi} \geqslant 0$, according to (49). Since $\beta_{ui} < 0$, a decrease in frequency is predicted: another indication of the slowing effect of ion transport. Even when r_{ur} is between 0·64 and 1, calculations using (47) show that ion transport produces a frequency decrease. In contrast, the calculations demonstrate that the damping rate β_r may either increase or decrease as a result of ion transport.

These results can be interpreted as consequences of two electrical effects. One is that a finite resistance to transport keeps ions from responding instantaneously to changes in electrochemical potential which accompany interfacial deformation. As a result, electrical forces which oppose the deforming forces and thus slow down the motion arise. This effect produces the frequency decrease for stable motion and contributes to the slower growth of unstable disturbances.

The second effect is a direct result of the irreversible nature of the transport processes. During deformation there is interconversion of electrical and mechanical energy. In view of the negative contribution of the diffuse layer to interfacial tension, it is clear that mechanical energy is produced as the perturbation amplitude increases and is removed as the amplitude decreases. Because of irreversibility, the interconversion process is accompanied by some dissipation of energy. Hence, the total electromechanical energy of the system decreases with time, producing a damping effect on stable wave motion and contributing to a decreased rate of growth of unstable disturbances.

Although irreversibility of ion transport acts to damp oscillatory motion, viscous dissipation must also be considered in determining the overall damping rate. Near the interface a type of boundary-layer flow exists (see Miller & Scriven

1968) and viscous dissipation in this region is decreased by the electrically produced reduction in oscillation frequency. When this effect is larger than the electrical damping effect the net result of ion transport is a decrease in damping rate. However, when the electrical damping effect is larger than the viscous effect, total damping rate increases.

Calculations based on (44) show that the ion transport effects described above are relatively small in magnitude, a few per cent at most, when potential drops Ψ_0 are sufficiently small for the Debye–Hückel approximation to apply (less than about 25 mV). The form of (45) suggests, however, that the effects increase rapidly with increasing Ψ_0 (note that they are independent of ionic strength since a_2 does not depend on the Debye length κ^{-1}). Although the present analysis should not really be used for large values of Ψ_0, it seems worth noting that, were (44) valid for aqueous diffuse layers having γ_{DL} in the 0·1–0·5 dyne/cm range (Ψ_0 in the 50–100 mV range), ion transport effects would cause reductions in oscillation frequency ranging from 15 to 45 %. These values are based on calculations with $a_1 = 10$, e.g. on values of the wavenumber α and total interfacial tension γ_T of 10 cm^{-1} and 0·02 dyne/cm or 100 cm^{-1} and 0·2 dyne/cm. Thus, the present work suggests that ion transport effects should be considered in interpreting capillary wave experiments in many low-tension systems. Indeed, if the general equations of ionic transport were solved numerically, such experiments could be used to provide quantitative information about the potential drop Ψ_0 and other electrical characteristics of low-tension interfaces.

Further understanding of the slowing effect of ion transport can be obtained by considering the case of inviscid fluids. Although the results for this case cannot be applied directly to any system of interest, the pertinent equations are simpler and easier to interpret than those derived above for viscous fluids. For in the absence of viscosity the dispersion equation (39) reduces to

$$\beta^2 = -\beta_p^{*2} + \frac{2\gamma_{DL}\kappa^2\alpha}{(\rho_1+\rho_2)\,[1-(\kappa/\alpha)hy_D^2]}\left\{h\left(1+\frac{\kappa}{\alpha}y_D^2-y_D^2\right)-1\right.$$
$$\left.+\frac{\kappa y_D^2\left[h\left(-3-2\dfrac{\alpha}{\kappa}+y_D^2\right)+\left(1+\dfrac{\alpha}{\kappa}\right)\left(1-\dfrac{\kappa}{\alpha}hy_D^2+2\dfrac{\alpha}{\kappa}\right)\right]}{2\alpha[1+(\kappa/2\alpha)y_D^2]\,(1+2\alpha/\kappa)}\right\}. \tag{50}$$

When there is no resistance to ion transport, i.e. when $\mathscr{D}\to\infty$, $y_D^2 = \beta/\mathscr{D}\kappa^2$ vanishes and (50) predicts undamped oscillatory motion when the interface is stable and aperiodic growth when it is unstable:

$$\beta = \pm i\beta_T^* \quad (\alpha/\kappa \ll 1). \tag{51}$$

However, when diffusion coefficients are relatively small as in aqueous solutions, electrical forces slow down stable wave motion so much that it is no longer oscillatory at all. Instead the interface returns aperiodically to the plane configuration after deformation. This can be seen by expanding (50) in powers of y_D^2 and (α/κ). The result is

$$\beta = \mathscr{D}\beta_T^{*2}(\rho_1+\rho_2)/2\gamma_{DL}\alpha. \tag{52}$$

According to (52), the interface moves slower as the mean diffusion coefficient becomes smaller, i.e. as resistance to transport increases. When there is no resistance to transport ($\mathscr{D} \rightarrow \infty$) or when there is no double layer at all ($\gamma_{DL} = 0$), this mode decays very rapidly and the oscillatory mode described by (51) would be observed experimentally.

The large slowing effect of electrical forces illustrated by the aperiodic result (52) is somewhat analogous to the slowing effect of a high fluid viscosity. In systems having no electric fields or double layers interfacial tension and gravity act to restore a wavy interface to the plane configuration. Opposing such motion are viscous stresses, which increase with both fluid viscosity and speed of motion. Since the total viscous force on an element of fluid cannot exceed the restoring force in magnitude, interfacial motion is very slow for fluids of extremely high viscosity. In a similar manner retarding electrical forces increase both with resistance to transport (i.e. with $\mathscr{D}^{-1}$) and with speed of motion. When $\mathscr{D}$ is small, the interfacial speed must be small to keep the retarding electrical force from exceeding the restoring force produced by interfacial tension and gravity.

In this connexion, it is of interest that transport effects associated with electrical conduction can influence wave motion and stability in hydromagnetic systems. Zadoff & Begun (1968) studied situations where a uniform magnetic field is applied parallel to a plane interface separating an inviscid fluid of low resistivity from a vacuum. When gravity does not influence stability, i.e. for a vertical interface, their analysis predicts oscillatory wave motion which, although undamped in the absence of resistivity, continuously decreases in amplitude when a finite resistance exists. When the interface is horizontal with a perfectly conducting fluid above the vacuum, the interface may be either stable or unstable. If the magnetic field is too small to overcome gravitational effects and stabilize the interface under these conditions, finite resistivity leads, according to the analysis, only to changes in disturbance growth rates. However, if the magnetic field is large enough to stabilize the interface of a perfectly conducting fluid, new modes of instability are sometimes found when finite resistivity is included. The reason is that the system is enabled to reach low energy states which are not accessible in the absence of electrical resistance.

Including effects of electrical resistance can also lead to new modes of instability in systems where electric instead of magnetic fields are applied, but where there are no double layers. Saville (1971) has shown that oscillatory modes of instability exist for fluid cylinders of finite resistivity in longitudinal electric fields which do not exist for perfectly conducting fluids. From a physical point of view, finite resistivity can slow down charge transport by conduction to such an extent that convective transport of charge along the interface becomes important. The resulting changes in interfacial charge distribution produce changes in electrical shear stresses which lead to the oscillatory modes of instability.

That electrical resistance effects can produce new modes of electrohydrodynamic instability in systems lacking double layers indicates that ion transport effects can, under appropriate conditions, do the same in systems having double layers. The analysis of this paper may be looked upon as an extension of existing electrohydrodynamic work on wave motion and stability (Melcher 1963; Melcher & Smith 1969) to include systems with diffuse layers. If transport of charge across the interface were incorporated into the present work, Melcher & Smith's (1969) results for a plane interface could be obtained as a special case of the generalized analysis by requiring the free charge density ρ_e to vanish uniformly. In a similar manner Saville's oscillatory modes of instability could, presumably, be derived by considering fluid cylinders with diffuse layers. These and other aspects of the electrohydrodynamics of systems with diffuse layers are matters for further research.

6. Aperiodic motion for short wavelengths

Equation (44) applies to wave motion of interfaces with aqueous diffuse layers when disturbance wavelengths are relatively long, about 0·05 cm or longer. Another approximate version of the dispersion equation can be developed for situations where wavelengths are much shorter – about 5×10^{-4} cm – but still considerably greater than the diffuse-layer thickness (10^{-6} cm). Under these conditions there is no oscillation but simply an aperiodic decay of wave amplitude, even in the absence of electrical effects. Because $y^2 = \beta\rho/\mu\alpha^2 \ll 1$ in this case, all terms in r in the dispersion equation can be expanded in powers of y^2. Again α/κ and y_D^2 are small and, when fluid densities and viscosities are assumed equal as before, (39) can be reduced, after considerable algebra, to

$$\beta = \frac{\beta_T^{*2}\rho}{2\mu\alpha^2(1+5\gamma_{DL}/4\mu\mathscr{D}\kappa)} = \frac{\beta_T^{*2}\rho}{2\mu\alpha^2(1+5\epsilon\Psi_0^2/32\pi\mu\mathscr{D})}. \tag{53}$$

When there is no resistance to transport ($\mathscr{D}\to\infty$) or no potential drop across the diffuse layer ($\gamma_{DL} = 0$), the second term inside the parentheses in the denominator is zero and (53) simplifies to the well-known expression for aperiodic motion of a viscous fluid when subjected to disturbances of short wavelengths (see Chandrasekhar 1961). For an aqueous diffuse layer with $\kappa^{-1} = 10^{-6}$ cm the requirement $|\beta/(\mathscr{D}\alpha\kappa)| \ll 1$ (see footnote at (38)) restricts applicability of (53) to situations where γ_T is less than about 0·1 dyne/cm. When $\gamma_T = 0.1$ dyne/cm, $\gamma_{DL} =$ 0·02 dyne/cm ($\Psi_0 = 22$ mV) and $\alpha = 10^4\,\text{cm}^{-1}$, (53) yields a time constant for decay of 5×10^{-5} s, a value about 25 % larger than that found when no resistance to ion transport exists. Thus, the slowing effect of ion transport found above for oscillatory motion extends to the aperiodic motion considered here, and, as before, the slowing effect increases rapidly with potential drop across the diffuse layer but is independent of the ionic strength. Unlike the earlier situation, however, the slowing effect is substantial even when Ψ_0 is relatively small, i.e. 22 mV. It should be larger still for systems having potential drops in the 50–100 mV range.

Rates of aperiodic damping obtained from (53) are not highly significant in themselves because the pertinent wavelengths and time constants are too small to be easily measured experimentally. What is of interest is that the same type of approximation can probably be used to determine the effect of ion transport on wave motion of soap films and other thin liquid films. The reason is that in such films aperiodic decay dominates over a wide range of conditions (Vrij *et al.* 1970).

7. Summary

An approximate solution of the equations describing convection and transport in a diffuse electrical double layer slightly perturbed from equilibrium has been obtained. The solution has been used to study two types of stable wave motion of low-tension interfaces with diffuse layers: damped oscillatory motion for wavelengths which are relatively long (greater than about 0·05 cm for aqueous diffuse layers) and damped aperiodic motion for much shorter wavelengths (about 5×10^{-4} cm in aqueous solutions). In both cases ion transport was found to have a slowing effect, reducing the frequency of oscillatory motion and the rate of damping of aperiodic motion. Consideration of unstable disturbances showed that their growth rates are slowed as well.

The results for oscillatory motion indicate that diffuse-layer effects should be considered in interpreting results of capillary wave experiments involving low-tension interfaces. The most interesting aspect of the results for aperiodic motion is their strong suggestion that ion transport may significantly influence aperiodic motion of thin liquid films having low interfacial tension.

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