

Influence of Evaporation on Ripples

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The viscoelastic properties of a liquid-vapor interface covered by a layer of surface active material are discussed in terms of the complex dilational modulus $\epsilon = d\sigma/d \ln \alpha$ where ϵ is the surface tension and α is the area of a surface element. This modulus is known to be closely related to the spectrum of surface waves. We allow for diffusion between the bulk liquid and the surfactant layer as well as for evaporation, i.e., mass transport between the surface and the vapor phase. Our result is a generalization of results by Lucassen and v.d. Tempel who neglected evaporation. For practical situations, contributions to ϵ from evaporation are about one order of magnitude smaller than those from diffusion in the liquid. We conclude that it will be almost impossible to get reliable data on evaporation from studies of the ripple spectrum.

Introduction

Evaporation plays an important role in many practical situations, for example, paint drying. This article is devoted to the question of whether ripples (also called capillary waves) on liquids are sensitive to evaporation. If so, then study of the ripple spectrum, for example by light scattering, might be an attractive new method to investigate evaporation.

The conventional theoretical treatment of surface waves¹⁻³ relates the ripple properties to the surface tension of the liquid, denoted by σ , and the viscoelastic properties of the surface described by the (complex) surface dilational modulus ϵ . This modulus gives the response of the surface to local compression and expansion:

$$\epsilon = d\sigma/d \ln \alpha \quad (1)$$

where α is the area of a surface element.

For pure liquids, $\epsilon = 0$. However, the presence of a layer of surface active material leads to surface elasticities that modify wave properties such as damping. We describe the surface layer by the surfactant adsorption, Γ , measured in mol cm⁻². Using the surface equation of state $\sigma = \sigma(\Gamma)$ one finds

$$\epsilon = \frac{d\sigma}{d \ln \Gamma} \frac{d \ln \Gamma}{d \ln \alpha} \quad (2)$$

If the total amount of adsorbed material does not change measurably during the lifetime of a ripple, $\Gamma\alpha = \text{constant}$ and

$$\epsilon = -\frac{d\sigma}{d \ln \Gamma} \equiv \epsilon_s \quad (3)$$

However, the surfactant layer is not always insoluble. A frequency dependence of ϵ may arise from relaxation mechanisms in the surface region. The best-studied mechanism is diffusional exchange of surfactant between the surface and the bulk liquid.^{4,5} In addition to this process, we permit evaporation, i.e., exchange of surfactant between the surface and the vapor phase.

Some General Results for Surface Waves

In the usual theory of surface waves, one calculates wavelike solutions of the linearized Navier-Stokes equations for an incompressible fluid subject to the appropriate boundary conditions. The details can be found in many texts on hydrodynamics; we give here only some general

results which are from the review by Lucassen.²

For simplicity, we restrict our discussion to the case of a liquid filling the half-space $y < 0$; its equilibrium surface is the plane $y = 0$. Denoting the x and y component of liquid velocity by u and v , one gets

$$u(x,y,t) = -ikAe^{ky} + mBe^{my}e^{i(kx+\omega t)} \quad (4)$$

$$v(x,y,t) = -kAe^{ky} - ikBe^{my}e^{i(kx+\omega t)} \quad (5)$$

where m is defined by

$$m^2 = k^2 + i\omega \frac{\rho}{\eta} \quad \text{Re } m > 0 \quad (6)$$

ρ and η are the density and the viscosity of the liquid which are assumed to be constants. Hence, when applying these results to the case of solutions with a nonuniform solute distribution, the solutions must be sufficiently dilute.

The ratio of A and B as well as the dispersion relation is determined by the stress boundary conditions, which state that the total stress at each point of the surface is zero. When the previous definitions are used, the final form of these equations is

$$\left(-i\omega\rho - 2\eta k^2 + i\frac{\sigma^{(0)}k^3}{\omega} + i\frac{\rho g k}{\omega} \right) A + \left(2i\eta k m + \frac{\sigma^{(0)}k^3}{\omega} + \frac{\rho g k}{\omega} \right) B = 0 \quad (7)$$

$$\left(-2i\eta k m - \frac{\epsilon k^3}{\omega} \right) A + \left(-\eta(k^2 + m^2) + i\epsilon \frac{mk^2}{\omega} \right) B = 0 \quad (8)$$

where g is the gravitational constant and $\sigma^{(0)}$ is the surface tension of the unperturbed surface.

So that a nontrivial solution for A and B is obtained, the determinant formed by the coefficients must be zero. This results in a relationship between the wave number k and the frequency ω , i.e., the dispersion relation.

For a pure frictionless liquid, we get the well-known result

$$\omega^2 = gk + \frac{k^3}{\rho} \quad (9)$$

(1) Levich, V. G. *Acta Physicochim. URSS* 1941, 14, 307, 321.

(2) Lucassen-Reynders, E. H.; Lucassen, J. *Adv. Colloid Interface Sci.* 1969, 2, 347.

(3) Hansen, R. S.; Ahmad, J. *Prog. Surf. Membr. Sci.* 1971, 4, 1.

(4) v. d. Tempel, M.; v. d. Riet, R. P. *J. Chem. Phys.* 1965, 42, 2769.

(5) Lucassen, J.; Hansen, R. S. *J. Colloid Interface Sci.* 1967, 23, 319.

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The corresponding surface waves have transverse character. We will concentrate on capillary waves. They have such a short wavelength that $k \gg (\rho g / \sigma)^{1/2}$; hence, the driving force is surface tension, and gravity can be neglected. Typical values for wave number and frequency are $k \approx 30 \text{ cm}^{-1}$ and $\omega \approx 200 \text{ s}^{-1}$. Under normal experimental conditions only these transverse capillary waves can be observed. For nonzero values of the viscosity and the surface dilatational modulus, however, the characteristic equation resulting from eq 7 and 8 has still another set of roots corresponding to capillary waves of longitudinal character.

As the experimental investigation of longitudinal capillary waves is rather complicated, they have escaped experimental observation until the work by Lucassen.⁶ He found the wavelengths of longitudinal waves to be about 30 times higher than those of transverse waves under the same experimental conditions.

As we are primarily interested in the dilational modulus ϵ , we note that longitudinal waves have propagation characteristics sensitive to ϵ for all values of ϵ while transverse waves are sensitive to ϵ only in the neighborhood of the maximum in the damping coefficient. For details the reader is referred to a review by Lucassen.²

The Dilational Modulus

In order to calculate the dilational modulus for a liquid covered by a soluble surfactant layer, we need an expression for $d \ln \Gamma / d \ln \alpha$ (see (2)). This can be derived from the condition of mass conservation at the surface. If we assume molecular diffusion in the liquid and the gas phase, this condition is

$$\frac{d(\Gamma\alpha)}{dt} = \alpha \left\{ D_2 \frac{\partial C_2}{\partial n} \Big|_s - D_1 \frac{\partial C_1}{\partial n} \Big|_s \right\} \quad (10)$$

where $C_{1,2}$ is surfactant concentration in the liquid and the gas phase, respectively, $D_{1,2}$ are the corresponding diffusion coefficients, n denotes the coordinate normal to the surface and subscript s means the function is evaluated at the surface.

From eq 10

$$\frac{d \ln \Gamma}{d \ln \alpha} = - \frac{d\Gamma/dt}{d\Gamma/dt + D_1 \partial C_1 / \partial n|_s - D_2 \partial C_2 / \partial n|_s} \quad (11)$$

The diffusion equations are

$$\frac{\partial C_1(x,y,t)}{\partial t} = D_1 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) C_1(x,y,t) - u(x,y,t) \frac{\partial}{\partial x} C_1(x,y,t) - v(x,y,t) \frac{\partial}{\partial y} C_1(x,y,t) \quad (12)$$

$$\frac{\partial C_2(x,y,t)}{\partial t} = D_2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) C_2(x,y,t) \quad (13)$$

If there is equilibrium between liquid and vapor in the absence of waves, the concentrations for a flat interface, denoted by superscript (0), will be homogeneous within both phases. Additional contributions due to ripples, denoted by superscript (1), will be sufficiently small so that we may neglect convection. We seek solutions of the form

$$C_1^{(1)}(x,y,t) = R_1 \exp[i(kx + \omega t) + q_1 y] \quad (14)$$

$$C_2^{(1)}(x,y,t) = R_2 \exp[i(kx + \omega t) - q_2 y] \quad (15)$$

where $q_{1,2}$ are defined by

$$q_{1,2}^2 = k^2 + i \frac{\omega}{D_{1,2}} \quad \text{Re } q_{1,2} > 0 \quad (16)$$

Furthermore, we need a relation between Γ and $C_1|_s$. While v.d. Tempel⁴ and Lucassen⁵ assumed equilibrium between the surface and the bulk liquid, i.e., Γ is a unique function of $C_1|_s$, we allow for an adsorption-desorption barrier at the interface:

$$-D_1 \frac{\partial C_1(x,y,t)}{\partial n} \Big|_s = k_1 C_1(x,y,t)|_s - k_{-1} \Gamma(x,t) \quad (17)$$

where in general k_1 and k_{-1} will depend on $C_1|_s$ and Γ . As we are only interested in small perturbations about a steady-state situation, we may assume k_1 and k_{-1} to be constants.

Values for k_1 and k_{-1} have been calculated by Christov et al.⁷ using experimental data of Lucassen.⁸⁻¹⁰ For an acidified decanoic acid solution, they get results for k_1 and k_{-1} depending on solute concentration, e.g., for $C_1 = 2 \times 10^{-8} \text{ mol/cm}^3$, $k_1 = 9.1 \times 10^{-4} \text{ cm/s}$ and $k_{-1} = 8.9 \times 10^{-2} \text{ s}^{-1}$. Equation 17 immediately yields

$$\Gamma^{(1)}(x,t) = \frac{k_1 + D_1 q_1}{k_{-1}} C_1^{(1)}(x,y,t)|_s \quad (18)$$

For $D_1 q_1 \ll k_1$ this reduces to the result of assuming equilibrium between Γ and $C_1|_s$.

The result for the dilational modulus is

$$\epsilon = \epsilon_s \left\{ 1 - i \frac{k_{-1} D_1 q_1}{\omega(k_1 + D_1 q_1)} \left(1 + \frac{D_2 q_2}{D_1 q_1} \frac{R_2}{R_1} \right) \right\}^{-1} \quad (19)$$

In the absence of evaporation of $R_2 = 0$ and we obtain essentially the same result as v.d. Tempel⁴ and Lucassen.⁵

In order to proceed, the ratio R_2/R_1 must be determined from an evaporation model. We will discuss two possibilities which have been introduced by others.

Hansen⁶ assumes an equilibrium distribution of surfactant between liquid and gas phases

$$C_2(x,y,t)|_s = \lambda C_1(x,y,t)|_s \quad (20)$$

Hence, $R_2/R_1 = \lambda$. λ is typically of the order 10^{-3} .

Brian⁷ assumes the relation

$$D_2 \frac{\partial C_2(x,y,t)}{\partial n} \Big|_s = \kappa (C_\infty - C_1|_s) \quad (21)$$

where C_∞ is the equilibrium value of C_1 , and κ is of the order $10^3 \text{ cm}^2 \text{ s}^{-1}$. This model leads to $R_2/R_1 = \kappa / D_2 q_2$.

For typical values of the parameters ($k = 30 \text{ cm}^{-1}$, $\omega = 200 \text{ s}^{-1}$, $D_1 = 10^5 \text{ cm}^2 \text{ s}^{-1}$, $D_2 = 10^{-1} \text{ cm}^2 \text{ s}^{-1}$), we find that contributions to ϵ from evaporation are about one magnitude smaller than those from diffusion in the liquid. This statement is independent of the relationship between Γ and C_1 , and we may assume equilibrium or an adsorption-desorption barrier at the surface. We conclude that diffusion dominates evaporation as the mechanism for restoring concentration gradients induced by ripples.

We have also investigated the transient case of waves on an evaporating liquid, e.g., on a drying paint film, when

(7) Christov, C. I.; Ting, L.; Wasan, D. T. *J. Colloid Interface Sci.* **1982**, *85*, 363.

(8) Lucassen, J.; v. d. Tempel, M. *J. Colloid Interface Sci.* **1972**, *41*, 491.

(9) Lucassen, J.; v. d. Tempel, M. *Chem. Eng. Sci.* **1972**, *27*, 1283.

(10) Lucassen, J.; Giles, D. J. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 217.

(11) Hansen, R. S. *J. Phys. Chem.* **1960**, *64*, 637.

(12) Brian, P. L. T. *AIChE. J.* **1971**, *17*, 765.

there are initial concentration gradients in both phases at the beginning of the ripple experiments. We, therefore, first solved eq 10, 12, 13, 17, 20, and 21, respectively, for a flat interface starting with a fresh interface at $t = 0$, i.e., $C_1(x,y,0) = C_0$ and $C_2(x,y,0) = 0$. We then assumed that quantities like $C_1^{(0)}(y,t)$, which now depend on time and location because of evaporation, do not change significantly on the time scale of ripples and calculated the perturbed concentration profile by an appropriate linearization procedure. So we determined $C_1^{(1)}$ from the equation [see (12)]

$$\frac{\partial C_1^{(1)}(x,y,t)}{\partial t} = D_1 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) C_1^{(1)}(x,y,t) - v(x,y,t) \frac{\partial}{\partial y} C_1^{(0)}(y,t_e) \quad (22)$$

where t_e is the time of observation.

For all practical situations, the initial concentration gradients lead to negligible deviations from the equilibrium results presented above. This can easily be understood: according to (14), perturbations of solute concentration decay on a length scale $|q_1|^{-1} \sim (D_1/\omega)^{1/2}$ while $C_1^{(0)}(t_0)$

changes on a length scale of $(D_1 t_e)^{1/2}$. Hence, initial gradients are of little importance for $(\omega t_e)^{1/2} \gg 1$ which holds for all experimental situations.

Conclusions

Our main result is expression 19 for the dilational index ϵ . We have shown that diffusion in the liquid dominates evaporation as the mechanism for restoring gradients in solute concentration. But even diffusion is of minor importance: Lucassen and Hansen⁵ have shown that it is already difficult to determine the diffusion coefficient from ripple experiments. Hence, our results suggest that it will be almost impossible to get reliable data on evaporation from studies of the ripple spectrum.

Similar equations can be applied to ripples at a liquid-liquid interface when discussing transfer of surfactant between the liquids. In that case, the additional terms in the expression for the dilational modulus will probably be more important, and the effect may be larger.

Acknowledgment. J.M.D. thanks Paul Meakin for stimulating his interest in this problem. This work was supported in part by the National Science Foundation and the Defense Research Projects Agency.

Thomson Equation Revisited in Light of Ion-Clustering Experiments

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(Received: September 25, 1981; In Final Form: March 29, 1982)

Gas-phase ion-clustering data are used to assess the validity of the classical approach to nucleation by comparing experimental values for various positive ions to those predicted by Thomson's charged liquid drop expression at small cluster sizes for water, ammonia, pyridine, acetonitrile, and methanol. While some data for water compare favorably, those for the other ligands do not. In many systems, the experimental results for the entropies are sharply more negative than those predicted, suggesting that many cluster ions have a more ordered structure than can be accounted for in the classical approach. This effect is apparently due to orientation of ligand molecules about the ion. Possible adjustments to bulk parameters in the Thomson equation at small cluster sizes are considered, but it is concluded that such adjustments will not lead to significant improvements in the expression. This suggests that a fundamental inconsistency exists between the general form of the classical expression and the properties of many small cluster ions. It is also shown that the "effective size" of the ligand molecules has an important effect on the calculated results.

Introduction

Studies pertaining to various classes of nucleation phenomena comprise a very active area of current research. At the present time, an understanding of the molecular aspects of nucleation is far from complete, and basic theories are in a continuing state of development.¹⁻⁶ The Thomson equation has been a successful model in computing the energy barrier to nucleation about ions for some substances, but not for many others.^{2c} The purpose of the present paper is to give much more extensive and general

consideration to this relationship than that given previously⁵ in terms of recent findings from experimental ion-clustering studies. Such an assessment is especially relevant now, in view of recently developed models based on statistical mechanical⁷ and electrostatic⁸ corrections to the

(1) A. A. Lushnikov and A. G. Sutugin, *Russ. Chem. Rev. (Engl. Transl.)*, **45**, 197 (1976) (*Usp. Khim.*, **45**, 385 (1976)).

(2) See: (a) A. C. Zettlemoyer, Ed., "Nucleation", Marcel Dekker, New York, 1969; (b) F. F. Abraham, "Homogeneous Nucleation Theory, The Pretransition Theory of Vapor Condensation, Supplement I", Academic Press, New York, 1974; (c) J. Heicklen, "Colloid Formation and Growth, A Chemical Kinetics Approach", Academic Press, New York, 1976.

(3) A. C. Zettlemoyer, Ed., *Adv. Colloid. Interface Sci.*, **7** (1977) (special issue on nucleation phenomena).

(4) F. C. Tompkins, Ed., "Precipitation", *Faraday Discuss. Chem. Soc.*, **61** (1976).

(5) A. W. Castleman, Jr., P. M. Holland, and R. G. Keesee, *J. Chem. Phys.*, **68**, 1760 (1978).

(6) A. W. Castleman, Jr., in "Advances in Colloid and Interface Science, 'Nucleation'", A. Zettlemoyer, Ed., Elsevier, Oxford, England, 1979, pp 73-128.

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[‡] The Cooperative Institute for Research in Environmental Sciences is jointly sponsored by the University of Colorado and the National Oceanic and Atmospheric Administration.